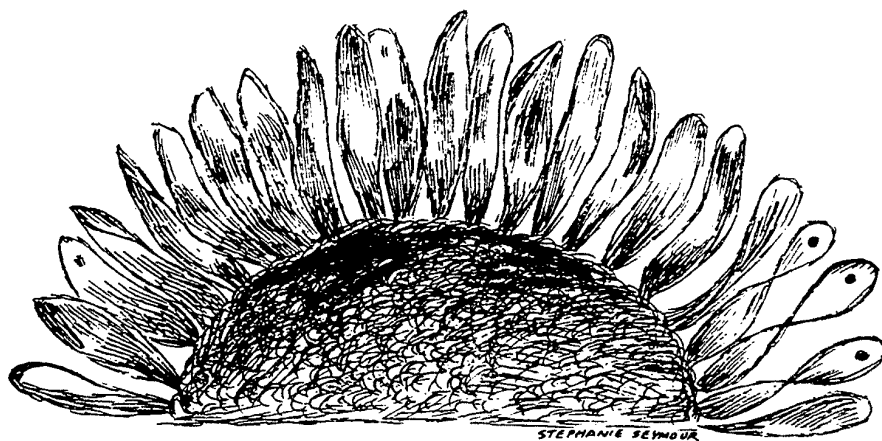


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# 26<sup>th</sup> International Symposium on Free Radicals



Assisi, Italy  
2-7 September 2001

## Book of Abstracts

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<p>ABSTRACT (Maximum 200 words)</p> <p>Sessions: 1/ <b>Reaction Dynamics: Experiment and Theory.</b> Reactivity of the O(<sup>1</sup>D) atom: from state-to-state dynamics to multiple pathway chemistry; Quantum dynamics on some atom-hydrogen insertion reactions; UV and near-UV photodissociation dynamics of small hydrocarbon free radicals. 2/ <b>Spectroscopy.</b> Some "radical" new experiments in molecular spectroscopy; Linear triatomic radicals containing transitions metal atoms: a case history of vibronic coupling; Fourier-transform microwave spectroscopy of the acetyl radical. 3/ <b>Astrochemistry.</b> Low temperature reactions of free radicals and their role in the chemistry of interstellar clouds; Fast-flow studies of the C+H<sub>2</sub>S, C<sup>2</sup>H<sup>2</sup> and C<sup>2</sup>H<sup>4</sup> reactions: A comparison between experimental and theoretical determinations of atomic hydrogen production; Detailed SACM modeling of the reactions O + OH ⇌ O<sub>2</sub> + H and O + OD ⇌ O<sub>2</sub> + D at 0 ≤ T ≤ 300 K. 4/ <b>Spectroscopy, Kinetics and Combustion.</b> Infrared laser spectroscopy and chemical kinetics of free radicals; Experimental and computational studies of free radical reactions of importance in combustion; Infrared frequency-modulation probing of product information in reactions of alkyl radicals with O<sub>2</sub>. 5/ <b>Molecular Ions.</b> Three-body breakup in dissociative recombination of molecular ions; Photoelectron-photofragment coincidence studies of the energetics and dynamics of alkoxy radicals; Laboratory and raio-astronomical spectroscopy of the hyperfine structure of N<sub>2</sub>D<sup>+</sup>. 6/ <b>Photodissociation.</b> Photodissociation of the free radicals HNCN and HCNN; Photoinitiated dissociation and isomerization of the hydroxymethyl radical; Inner-shell studies of free radicals and transient species by Synchrotron radiation. 7/ <b>Spectroscopy and Stereodynamics.</b> Laser spectroscopy of free radicals in hydrocarbon oxidation; Sterodynamics of OH; State-to-state inelastic collisional energy transfer in electronically excited CH radicals. 8/ <b>Reaction Dynamics and Spin-Orbit Effects.</b> Theoretical studies of electronically non-adiabatic effects in reactions of halogens: F+HD→HF+D and Cl+H<sub>2</sub>→HCl+H; Vibrational state resolved studies of reactive and inelastic collision dynamics; Quasiclassical trajectory studies of the dynamics and sterodynamics of the OH+H<sub>2</sub>→H+H<sub>2</sub>O and the reverse action. 9/ <b>Atmospheric Chemistry.</b> Free radicals, short-lived compounds, and their impact on the Earth's atmosphere; Intermediates in proton transfer and nucleophilic bimolecular substitution (S<sub>N</sub>2) reactions: a theoretical study; Determination of the 0 K enthalpies of formation of radical cations by TPEPICO spectroscopy: application to CF<sub>3</sub><sup>+</sup>, C<sub>2</sub>F<sub>5</sub><sup>+</sup>, C<sub>3</sub>F<sub>7</sub><sup>+</sup>, and SF<sub>5</sub><sup>+</sup>. 10/ <b>Intermolecular Interactions and Energy Transfer.</b> Production and characterization of open shell atom and free radical beams: a systematic study of intermolecular forces from scattering experiments; Ion imaging study of the inelastic scattering of NO with Ar; State-resolved electronic energy transfer in CN(A<sup>2</sup>II)-Ar and He collisions: High rationale levels. 11/ <b>IR Spectroscopy in He Nanodroplets and Photodissociation.</b> Free radical complexes in Helium nanodroplets: High resloution infrared spectroscopy; Molecular beam studies of the competing bond fission channels of isomerically selected radicals: allyl, 2-propenyl, and 1-propenyl radicals; Photodissociations of the OH radical using velocity map imaging. 12/ <b>Free Radical Reactions.</b> Laser studies of free radical reactions – from diatomics to DNA; Barrierless reactions: Radical products and radical ideas; High resolution ZEKE-photoelectron spectroscopy of hydrocarbon radicals. 13/ <b>Spectroscopy, Dynamics and Kinetics of Free Radicals.</b> An injection seeded, single frequency optical parametric oscillator for high resolution molecular spectroscopy; High resloution IR laser studies of radicals: Spectroscopy and reaction dynamics; Studying reaction intermediates and reaction dynamics/kinetics with time-resolved Fourier-transform spectroscopy.</p>				
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# **26<sup>th</sup> International Symposium on Free Radicals**

**“La Cittadella”  
ASSISI, Italy**

**2-7 September 2001**

***Chair:***

Prof. Piergiorgio Casavecchia  
Dipartimento di Chimica  
Università di Perugia  
06123 Perugia, Italy  
[piero@dyn.unipg.it](mailto:piero@dyn.unipg.it)



## **SYMPOSIUM PROGRAMME AND ABSTRACTS**

AQ F02-06-1093

# 26<sup>th</sup> International Symposium on Free Radicals

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Fax (+39) 075 812445

<http://www.chm.unipg.it/chimgen/mb/cong/FreeRadicals2001.html>



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**26<sup>th</sup> International Symposium on Free Radicals:**

- Università degli Studi di Perugia
- Dipartimento di Chimica, Università di Perugia
- Italian National Research Council (C.N.R.)
- U.S. Army Research Laboratory - European Research Office (ARL-ERO)
- Comune di Assisi

## Foreword

The International Free Radical Symposium was established over 40 years ago to bring together workers at the frontier of research in a wide variety of areas of free radical chemistry with particular emphasis on the spectroscopic identification, characterization and dynamics of radicals. Continuing progress in our understanding of free radical chemistry, and the importance of this topic, have provided the impetus for a series of successful conferences, dating back to 1956. The conferences have taken place biannually, with the exception of the first four editions which were held annually, in alternation between North America, Europe and Asia. This alternation underlines the international aspect of the field and provides a regular channel for exchange between scientists in North America, Europe, Asia, and Southern Hemisphere. The dates of previous symposia on Free Radicals in this series, sites, and organizers are listed in the next page. The University of Perugia is honored to host the 26<sup>th</sup> symposium of the series, which is the second to have been held in Italy, after Padova in 1965.

The purpose of the 2001 symposium is to survey recent advances, undertake stimulating discussions, generate new ideas, and map out future directions in the field of free radicals. The interest in this field has grown strongly as a result of the application of laser techniques in free radical research. The short-living radicals can be probed by sensitive laser diagnostic methods like laser-induced-fluorescence (LIF), infrared (IR) absorption or resonant enhanced multiphoton ionization (REMPI), their dynamics can be studied with femtosecond time resolution and in crossed beams. New aspects of free radical kinetics and dynamics can be explored in liquid helium nanodroplets. Two-dimensional distributions of radicals in flames can be visualized by a single laser pulse. In addition, lasers are applied successfully for the production of free radicals by laser photolysis or laser vaporization. Many free radicals have been produced and/or observed for the first time by using lasers. Pulsed and continuous electrical discharges in supersonic expansion have expanded the ways of generating a variety of intense radical beams for spectroscopy and dynamics studies. A second reason for the increased interest in this field is the role of free radicals in atmospheric chemistry in relation to environmental problems. The study of radical intermediates in combustion processes is also extremely important. Finally, a great impetus to free radical research has been given by the observations of these species in interstellar space.

It is clear from the above that the Free Radical Symposia are strongly interdisciplinary with chemists, physicists and astrophysicists participating. This makes the conference so unique; there are no other series of meetings like this one. Related conferences are focused on either molecular spectroscopy or molecular dynamics. The main benefits of this conference arise from contacts between experimental and theoretical scientists working in different disciplines, chemistry, physics, astrophysics, and environmental science.

We would like to thank the sponsors of the symposium for their support. In particular we thank all the invited speakers for agreeing to participate in the symposium, and all the participants, both chemists and physicists, experimentalists and theorists, coming from more than 15 foreign countries. Finally, we wish to thank all the members of the local organizing committee and in particular Nadia Balucani and Laura Cartechini for their dedication to the organization of the Symposium, Giovanni Capozza and Enrico Segoloni for their help in the editing of the book of abstracts, and Stefano Crocchianti and David Cappelletti for website assistance.

Piergiorgio Casavecchia

## Symposium History

<i>Date</i>	<i>Location</i>	<i>Symposium Chair(s)</i>
1956	Quebec City, CANADA	P. A. Giguère
1957	Washington, DC, USA	H. P. Broida, A. M. Bass
1958	Sheffield, UK	G. Porter
1959	Washington, DC, USA	H. P. Broida, A. M. Bass
1961	Uppsala, SWEDEN	S. Claesson
1963	Cambridge, UK	B. A. Trush
1965	Padua, ITALY	G. Semerano
1967	Novosibirsk, USSR	V. N. Kondratiev
1969	Banff, CANADA	H. Gunning, D. A. Ramsay
1971	Lyon, FRANCE	M. Peyron
1973	Königsee, GERMANY	W. Groth
1976	Laguna Beach, CA, USA	E. K. C. Lee, F. S. Rowland
1977	Lyndhurst, Hants, UK	A. Carrington
1979	Sanda, Hyogo-ken, JAPAN	Y. Morino, I. Tanaka
1981	Ingonish, NS, CANADA	W. E. Jones
1983	Lauzelles-Ottignies, BELGIUM	R. Colin
1985	Granby, Colorado, USA	K. M. Evenson, R. F. Curl, H. E. Radford
1987	Oxford, UK	J. M. Brown
1989	Dalian, CHINA	Postponed
1990	Susono, Shizuoka, JAPAN	H. Hirota
1991	Williamstown, MA, USA	S. D. Colson
1993	Doorworth, NETHERLANDS	H. ter Meulen
1995	Victoria, BC, CANADA	A. J. Merer
1997	Tällberg, SWEDEN	M. Larsson
1999	Flagstaff, AZ, USA	T. A. Miller
2001	Assisi, ITALY	P. Casavecchia

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# 26<sup>th</sup> International Symposium on Free Radicals

## Programme

### Sunday, 2 September 2001

15:00-19:30      Registration at conference desk

20:00      *Welcome Dinner*

### Monday, 3 September 2001

8:50-9:00      Introduction - **P. Casavecchia**

<b>SESSION 1:</b>	<b>"Reaction Dynamics: Experiment and Theory"</b> (Session Chair: <b>J. M. Brown</b> )
-------------------	---

9:00-9:40      **X. Yang** (Institute of Atomic and Molecular Sciences,  
Academia Sinica, Taipei, and National Tsing-Hua University,  
Hsinchu, Taiwan)  
***Reactivity of the O(<sup>1</sup>D) atom: From state-to-state  
dynamics to multiple pathway chemistry***

9:40-10:20      **J.-M. Launay** (University of Rennes, Rennes, France)  
***Quantum dynamics on some atom-hydrogen insertion  
reactions***

10:20-10:40      Hot topic:  
**J. Zhang**  
***UV and near-UV photodissociation dynamics of small  
hydrocarbon free radicals***

10:40-11:10 *Coffee break*

<b>SESSION 2:</b>	<b>"Spectroscopy"</b> (Session Chair: <b>T. Amano</b> )
-------------------	---

- 11:10-11:50      **R. J. Saykally** (University of California, Berkeley, CA, USA)  
*Some "radical" new experiments in molecular spectroscopy*
- 11:50-12:30      **A. J. Merer** (University of British Columbia, Vancouver, Canada)  
*Linear triatomic radicals containing transition metal atoms: a case history of vibronic coupling*
- 12:30-12:50      Hot topic:  
**E. Hirota**, A. Mizoguchi, Y. Ohshima, Y. Sumiyoshi, and Y. Endo  
*Fourier-transform microwave spectroscopy of the acetyl radical*
- 13:10              Lunch

<b>SESSION 3:</b>	<b>"Astrochemistry"</b> (Session Chair: <b>B. A. Trush</b> )
-------------------	--

- 17:00-17:40      **I. W. M. Smith** (University of Birmingham, Birmingham, UK)  
*Low temperature reactions of free radicals and their role in the chemistry of interstellar clouds*
- 17:40-18:00      Hot topic:  
**A. Bergeat** and J.-C. Loison  
*Fast-flow studies of the C+H<sub>2</sub>S, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> reactions: A comparison between experimental and theoretical determinations of atomic hydrogen production*
- 18:00-18:20      Hot topic:  
A. I. Maergoiz, **J. Troe**, and V. G. Ushakov  
*Detailed SACM modeling of the reactions  $O + OH \rightleftharpoons O_2 + H$  and  $O + OD \rightleftharpoons O_2 + D$  at  $0 \leq T \leq 300$  K*
- 18:20-19:40      Oral (1'30") poster presentations (**P1-P45**)
- 20:00              Dinner
- 21:15              Poster session (**P1-P45**)

**Tuesday, 4 September 2001**

<b>SESSION 4:</b>	<b>"Spectroscopy, Kinetics and Combustion"</b> (Session Chair: <b>J. P. Maier</b> )
-------------------	--

- 9:00-9:40        **R. F. Curl** (Rice University, Houston, TX, USA)  
*Infrared laser spectroscopy and chemical kinetics of free radicals*

9:40-10:20 **M. J. Pilling** (University of Leeds, Leeds, UK)  
***Experimental and computational studies of free radical reactions of importance in combustion***

10:20-10:40 Hot topic:  
 J. D. DeSain, E.P. Clifford, and **C. A. Taatjes**  
*Infrared frequency-modulation probing of product formation in reactions of alkyl radicals with O<sub>2</sub>*

10:40-11:10 *Coffee break*

<b>SESSION 5:</b>	<b>"Molecular Ions"</b> (Session Chair: <b>A. Dalgarno</b> )
-------------------	--

11:10-11:50 **M. Larsson** (Stockholm University, Stockholm, Sweden)  
***Three-body breakup in dissociative recombination of molecular ions***

11:50-12:30 **R. E. Continetti** (University of California, San Diego, CA, USA)  
***Photoelectron-photofragment coincidence studies of the energetics and dynamics of alkoxy radicals***

12:30-12:50 Hot topic:  
**L. Dore**, S. Beninati, G. Cazzoli, and P. Caselli  
*Laboratory and radio-astronomical spectroscopy of the hyperfine structure of N<sub>2</sub>D<sup>+</sup>*

13:10 *Lunch*

<b>SESSION 6:</b>	<b>"Photodissociation"</b> (Session Chair: <b>G. B. Ellison</b> )
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17:00-17:40 **D. M. Neumark** (University of California, Berkeley, CA, USA)  
***Photodissociation of the free radicals HNCN and HCNN***

17:40-18:00 Hot topic:  
 L. Feng, O. Khodykin, and **H. Reisler**  
*Photoinitiated dissociation and isomerization of the hydroxymethyl radical*

18:00-18:20 Hot topic:  
 M. Alagia, R. Richter, and **S. Stranges**  
*Inner-shell studies of free radicals and transient species by Synchrotron radiation*

18.20-19:40 Oral (1'30") poster presentations (**P46-P90**)

20:00 *Dinner*

21:15 Poster session (**P46-P90**)

**Wednesday, 5 September 2001**

<b>SESSION 7:</b>	<b>"Spectroscopy and Stereodynamics"</b> (Session Chair: <b>P. F. Bernath</b> )
-------------------	--

9:00-9:40      **T. A. Miller** (Ohio State University, Columbus, OH, USA)  
***Laser spectroscopy of free radicals in hydrocarbon oxidation***

9:40-10:20      **H. H. J. ter Meulen** (Universiteit Nijmegen, Nijmegen, The Netherlands)  
***Stereodynamics of OH***

10:20-10:40      Hot topic:  
 C. Murray, H. J. Crichton, and **K. G. McKendrick**  
*State-to-state inelastic collisional energy transfer in electronically excited CH radicals*

10:40-11:10 *Coffee break*

<b>SESSION 8:</b>	<b>"Reaction Dynamics and Spin-Orbit Effects"</b> (Session Chair: <b>V. Aquilanti</b> )
-------------------	--

11:10-11:50      **M. H. Alexander** (University of Maryland, College Park, MD, USA)  
***Theoretical studies of electronically non-adiabatic effects in reactions of halogens:  $F+HD \rightarrow HF+D$  and  $Cl+H_2 \rightarrow HCl+H$***

11:50-12:30      **H. F. Davis** (Cornell University, Ithaca, NY, USA)  
***Vibrational state resolved studies of reactive and inelastic collision dynamics***

12:30-12:50      Hot topic:  
 M. J. Lakin, D. Troya, G. Pota, **G. Lendvay**, M. Gonzales, and G. C. Schatz  
*Quasiclassical trajectory studies of the dynamics and stereodynamics of the  $OH+H_2 \rightarrow H+H_2O$  and the reverse reaction*

13:10      *Lunch*

Afternoon      Excursion to Perugia

20:00      *Dinner*

21:15-22:00      Oral (1'30") poster presentations (**P91-P125**)

22:00      Poster session (**P91-P125**)



**Thursday, 6 September 2001**

<b>SESSION 9:</b>	<b>"Atmospheric Chemistry" (Session Chair: L. F. Phillips)</b>
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- 9:00-9:40      **A. R. Ravishankara** (NOAA & University of Colorado, Boulder, USA)  
*Free radicals, short-lived compounds, and their impact on the Earth's atmosphere*
- 9:40-10:20      **P. Botschwina** (University of Goettingen, Goettingen, Germany)  
*Intermediates in proton transfer and nucleophilic bimolecular substitution ( $S_N2$ ) reactions: a theoretical study*
- 10:20-10:40      Hot topic:  
 R. Y. L. Chim, R. A. Kennedy, G. K. Jarvis, **R. P. Tuckett** and W. Zhou  
*Determination of the 0 K enthalpies of formation of radical cations by TPEPICO spectroscopy: application to  $CF_3^+$ ,  $C_2F_5^+$ ,  $C_3F_7^+$ , and  $SF_5^+$*
- 10:40-11:10      *Coffee break*

<b>SESSION 10:</b>	<b>"Intermolecular Interactions and Energy Transfer" (Session Chair: Y. Endo)</b>
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- 11:10-11:50      **F. Pirani** (Universita' di Perugia, Perugia, Italy)  
*Production and characterization of open shell atom and free radical beams: a systematic study of intermolecular forces from scattering experiments*
- 11:50-12:30      **D. W. Chandler** (Sandia National Labs, Livermore, CA, USA)  
*Ion imaging study of the inelastic scattering of NO with Ar*
- 12:30-12:50      Hot topic:  
**P. J. Dagdigan**, B. Nizamov, X. Yang, and M. H. Alexander  
*State-resolved electronic energy transfer in  $CN(A^2\Pi)$ -Ar and He collisions: High rotational levels*
- 13:10              *Lunch*

<b>SESSION 11:</b>	<b>"IR spectroscopy in He Nanodroplets and Photodissociation" (Session Chair: M. Jacox)</b>
--------------------	---

- 16:20-17:00      **R. E. Miller** (University of North Carolina, Chapel Hill, NC, Usa)  
*Free radical complexes in Helium nanodroplets: High resolution infrared spectroscopy*

- 17:00-17:40 **L. J. Butler** (University of Chicago, Chicago, IL, USA)  
***Molecular beam studies of the competing bond fission channels of isomerically selected radicals: allyl, 2-propenyl, and 1-propenyl radicals***
- 17:40-18:00 Hot topic:  
**D. H. Parker**, J. J. ter Meulen, W. Ubachs  
*Photodissociation of the OH radical using velocity map imaging*
- 19:00-20:00 Concert (Basilica Superiore S. Francesco)
- 20:30 Symposium Dinner

### **Friday, 7 September 2001**

<b>SESSION 12:</b>	<b>"Free Radical Reactions"</b> (Session Chair: <b>R. Colin</b> )
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- 9:00-9:40 **J. Wolfrum** (University of Heidelberg, Heidelberg, Germany)  
***Laser studies of free radical reactions - from diatomics to DNA***
- 9:40-10:20 **C. Wittig** (University of Southern California, Los Angeles, CA, USA)  
***Barrierless reactions: Radical products and radical ideas***
- 10:20-10:40 Hot topic:  
**I. Fisher**, T. Gilbert, and P. Chen  
*High-resolution ZEKE-photoelectron spectroscopy of hydrocarbon radicals*
- 10:40-11:10 Coffee break

<b>SESSION 13:</b>	<b>"Spectroscopy, Dynamics and Kinetics of Free Radicals"</b> (Session Chair: <b>A. Carrington</b> )
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- 11:10-11:30 Hot topic:  
J. A. J. Fitzpatrick, R. Burrows, O.V. Chekhlov, J. M. F. Elks, **C. M. Western**, and S. H. Ashworth  
*An injection seeded, single frequency optical parametric oscillator for high resolution molecular spectroscopy*
- 11:30-12:10 **D. J. Nesbitt** (JILA & University of Colorado, Boulder, CO, USA)  
***High resolution IR laser studies of radicals: Spectroscopy and reaction dynamics***

12:10-12:50	<b><u>Y.-P. Lee</u></b> (National Tsing-Hua University, Hsinchu, Taiwan) <b><i>Studying reaction intermediates and reaction dynamics/kinetics with time-resolved Fourier-transform spectroscopy</i></b>
12:50-13:00	Concluding remarks - <b>P. Casavecchia</b>
13:00	<i>Lunch</i>
Afternoon	Dispersal

**LIST  
OF  
INVITED LECTURES  
AND  
CONTRIBUTED PAPERS**

**I** = Invited Lectures

**H** = Hot Topics

**P** = Posters

<b>I-1</b> <b>Reactivity of the O(<sup>1</sup>D) atom: from state-to-state dynamics to multiple pathway chemistry</b> <u>X. Yang</u>	<i>p.1</i>
<b>I-2</b> <b>Quantum dynamics of some atom-hydrogen insertion reactions</b> <u>J.-M. Launay and P. Honvault</u>	<i>p.2</i>
<b>I-3</b> <b>Some "radical" new experiments in molecular spectroscopy</b> <u>R. J. Saykally</u>	<i>p.3</i>
<b>I-4</b> <b>Linear triatomic radicals containing transition metal atoms: a case history of vibronic coupling</b> <u>A. J. Merer</u>	<i>p.4</i>
<b>I-5</b> <b>Low temperature reactions of free radicals and their role in the chemistry of interstellar clouds</b> <u>I. W. M. Smith</u>	<i>p.5</i>
<b>I-6</b> <b>Infrared laser spectroscopy and chemical kinetics of free radicals</b> <u>R. F. Curl</u>	<i>p.6</i>
<b>I-7</b> <b>Experimental and computational studies of free radical reactions of importance in combustion</b> <u>M. J. Pilling</u>	<i>p.7</i>
<b>I-8</b> <b>Three-body breakup in dissociative recombination of molecular ions</b> <i>S. Datz, R. Thomas, S. Rosén, <u>M. Larsson</u>, A. M. Derkatch, F. Hellberg, and W. van der Zande</i>	<i>p.8</i>
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**ABSTRACTS  
OF  
INVITED LECTURES**

## Reactivity of the O(<sup>1</sup>D) Atom: From State-to-State Dynamics to Multiple Pathway Chemistry

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### Abstract

In this talk, we will present recent experimental results of two prototype reactions: the O(<sup>1</sup>D) reactions with H<sub>2</sub> and CH<sub>4</sub>. Rydberg "tagging" time-of-flight (TOF) technique has been applied to the investigations of the O(<sup>1</sup>D) + H<sub>2</sub> (HD, D<sub>2</sub>) → OH (OD) + H(D) reaction with very high translational energy resolution and sensitivity. Total product angular distribution at 1.3 kcal/mol energy indicates that total reaction products are forward and backward symmetric. However, quantum state resolved TOF data show that rotational state distribution seems not exactly forward and backward symmetric. Rotational excitation of H<sub>2</sub> seems to have a significant effect on the product (OH) state distribution and total reaction cross section. Rotationally excited H<sub>2</sub>(J=1) is less reactive than H<sub>2</sub>(J=0). State specific dynamics have been observed for the O(<sup>1</sup>D) + HD reaction at low collisional energy, in which low vibrationally excited OD(v=1,2) products seem to be forward scattered, while highly vibrationally excited OD(v=5,6) products are backward scattered. These new results provide an excellent testing ground for *ab initio* dynamical studies on this important system, and will be important for the elucidation of the insertion mechanism at the state-to-state level.

The O(<sup>1</sup>D) + CH<sub>4</sub> reaction has been reinvestigated using improved universal crossed molecular beam method. Angular resolved time-of-flight (TOF) spectra have been measured for various reaction channels of this reaction: OH+CH<sub>3</sub>, H+H<sub>2</sub>COH/H<sub>3</sub>CO, and H<sub>2</sub>+HCOH/H<sub>2</sub>CO. Different product angular distributions have been observed for these product channels, indicating that these reaction channels occur via distinctive dynamical pathways. This study provides an excellent example of multiple dynamical pathways in a single chemical reaction, which opens enormous opportunities in investigating the dynamics of complicated chemical reactions that are important in combustion and atmospheric chemistry, and also provide a link between kinetics studies and dynamical researches.

# QUANTUM DYNAMICS OF SOME ATOM-HYDROGEN INSERTION REACTIONS

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Quantum reactive scattering calculations for several insertion reactions involving metastable atoms ( $\text{N}(^2\text{D}) + \text{H}_2 \rightarrow \text{NH} + \text{H}$  [1],  $\text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$  [2] and  $\text{C}(^1\text{D}) + \text{H}_2 \rightarrow \text{CH} + \text{H}$  [3]) have been recently performed. Accurate *ab initio* potential energy surfaces have been used and the nuclear dynamics has been studied using a time-independent formalism and body-frame hyperspherical coordinates.

Because of their high exoergicity and large well depth (several eV), the quantum dynamical calculations for these reactions are more difficult than for abstraction reactions, such as  $\text{F} + \text{H}_2 \rightarrow \text{FH} + \text{H}$ .

Integral and differential cross sections have been obtained at several energies up to 150 meV. In general, we find a forward-backward symmetry in differential cross sections which is characteristic of a complex formation. The effect of initial rotational excitation of the  $\text{H}_2$  molecule has also been studied. The statistics of  $|S_{ij}|^2$  matrix elements has been analysed [4]. Their histogram follows rather closely a Poisson distribution which is characteristic of a chaotic regime in quantum collisional dynamics.

A detailed comparison between our results and recent experimental studies on the above reactions [5, 6, 7, 8] will be presented.

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26<sup>th</sup> INTERNATIONAL SYMPOSIUM ON FREE RADICALS  
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Some "Radical" New Experiments in Molecular Spectroscopy

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ABSTRACT

Cavity Ringdown Spectroscopy has been extended into the infrared with high resolution capabilities by employing an Alexandrite laser (700 – 800 nm) and stimulated Stokes scattering in H<sub>2</sub> to generate broadly tunable radiation. Doppler-limited linewidths near 150 MHz are measured for rovibrational transitions in the  $\nu_6$  band of the C<sub>9</sub> carbon cluster in a planar supersonic jet near 2014 cm<sup>-1</sup>, similar to those observed using diode lasers(1). Studies of other carbon clusters are in progress.

Single Photon InfraRed Emission Spectroscopy(SPIRES), developed for measuring IR emission spectra of laser-excited PAH molecules(2) with the sensitivity of single photon counting, has been extended to the PAH radical cation Pyrene<sup>+</sup> by incorporating an ion beam and reflectron into the apparatus(3). The SPIRES spectra of this ion exhibit the main features found in the astrophysical UIR bands, supporting the contention that PAH cations are largely responsible for these features(4).

A large number of lasing transitions have been found near 7 microns in pulsed supersonic discharges through a water/He mixture contained inside an optical supercavity(5). Some of these can be assigned to excited vibrational states of water, but many remain unassigned. We propose that the population inversion is generated through the production of H<sub>2</sub>O "from the top down" via ion-electron dissociative recombination of H<sub>3</sub>O<sup>+</sup> ions, and that this mechanism may operate in natural environments as well. Moreover, this proposed pumping mechanism may be fairly general, and could lead to a means of measuring product state distributions for dissociative recombination reactions.

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## Linear triatomic radicals containing transition metal atoms: a case history of vibronic coupling

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Laser-induced fluorescence spectra in the visible and near infra-red regions have recently been obtained for a number of linear triatomic molecules containing transition metal atoms. The spectra were recorded following the reaction of laser-ablated metal vapour with an oxidant gas such as methane, ammonia, water or cyanogen under supersonic jet-cooled conditions. Because of the comparatively large density of electronic states resulting from the open *d* shells of the metals, vibronic coupling between close-lying states is very common. In linear molecules this takes the form of coupling through the degenerate bending vibration between states that differ by one unit in their orbital angular momentum. The usual vibrational selection rules break down severely, so that both parallel and perpendicularly polarized bands appear in the same electronic transition. Perturbations caused by high vibrational levels of unseen lower-lying electronic states are widespread in the excited states; these vary from small local disruptions of the rotational structure to cases where a single vibrational level is split into several components scattered over more than 100 cm<sup>-1</sup>. In extreme cases the vibronic coupling is so strong that the lower of two interacting electronic states is distorted to a non-linear equilibrium configuration.

One of the families of molecules that we have studied is the metal methylidyne, which are compounds with the formula MCH made by reaction with methane. It appears that these are only formed by metals in Groups 4-6 of the periodic table. Group 3 metals, such as Y and La, do not form methylidynes under our experimental conditions, though they react readily with ammonia and water to form MNH and MOH compounds. Work is just beginning on the metal monocyanides. We find that nickel cyanide has the structure NiCN rather than NiNC, and that its electronic states cluster into "supercomplexes" resembling those found in NiH.

## Low Temperature Reactions and the Role of Free Radicals in the Interstellar Medium

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In this lecture, I shall review the latest progress in measuring rate coefficients for bimolecular reactions between neutral free radicals and neutral molecules by both the continuous flow CRESU (Cinétique de Réactions en Ecoulement Supersonique Uniforme) technique and the pulsed Laval nozzle method. Results will be presented for reactions of  $C(^3P)$  atoms and  $C_2H$  radicals and in both cases comparisons will be made with the results from recent crossed molecular beam experiments.

The laboratory measurements will be placed within the context of astrophysical chemistry. Over 120 molecules have now been identified in the interstellar medium, most of them in cold, dark, molecular clouds. Many of the observed species are free radicals and it is now clear that reactions between pairs of radicals and between radicals and unsaturated molecules must play an important part in the chemistry of these gigantic interstellar environments.

Ideally, models of the chemistry of interstellar clouds would require huge tables of rate constants and photochemical information obtained under conditions appropriate to the interstellar clouds. In practice, the only way forward is to use the limited amount of data available from experimental measurements and theoretical calculations to make sensible predictions of the rate coefficients for other reactions. Efforts in this direction are under way and the results will be summarised in the last part of this talk.

## Infrared Laser Spectroscopy and Chemical Kinetics of Free Radicals

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Our research has two aims: the observation and analysis of the infrared spectra of free radicals and the investigation of their chemical kinetics. The radical, HCCN, is an interesting example of a quasilinear molecule. *Ab initio* calculations predict that the CC and CN bond distances change significantly as HCC bond angle is bent from linearity. Several of the excited states associated with the HCC bend have been observed using infrared kinetic spectroscopy giving the energies of the bending levels. These energies have been used to determine an approximate potential function for the HCC bending motion. The variations in bond length with HCC angle predicted *ab initio* are indeed needed in order to reproduce the dependence of the rotational constants upon bending state. The infrared kinetic spectroscopy method is also used to explore radical kinetics. Some recent chemical kinetics studies will be described.

## Experimental and computational studies of free radical reactions of importance in combustion

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Modelling combustion processes requires an understanding of the kinetics and mechanisms of elementary reactions of free radicals over a wide range of conditions of temperature and pressure. Key issues include the precision and accuracy of the data, extrapolations beyond the experimental range obtainable in the laboratory and product yields in the case of multichannel reactions. *Ab initio* calculations and master equation models play an increasing role, along side experiment. Several reaction systems will be examined to illustrate key issues facing combustion chemists.

- **Reactions of large alkyl radicals.** Alkyl radicals are central to many combustion processes, over a wide range of temperatures. Key issues are the rates of decomposition and isomerisation, which determine the types of alkyl radicals reacting with  $O_2$  in combustion systems. Results will be presented for pentyl radicals, based on *ab initio* calculations of the transition states for decomposition and isomerisation and master equation calculations over a wide range of temperatures and pressures. At low T, the rate parameters can be expressed in conventional form, using the Troe representation. At higher temperatures, as has been previously recognised by Tsang, the rate coefficients, as conventionally defined, become time dependent and new representations become necessary.
- **Sulfur chemistry in combustion systems.** Sulfur plays a significant role in combustion processes influencing  $NO_x$  production and the formation of aerosols in aircraft contrails. Two key reactions are  $H + SO_2$  and  $OH + SO_2$ . Results will be presented that seek to resolve important issues in high temperature S chemistry, based on both experiment and master equation models. Sulfur and nitrogen chemistry are closely linked in the reactions of the NS radical, which have been little studied. Results and experiments and of *ab initio* calculations will be presented for  $NS + NO_2$

### THREE-BODY BREAKUP IN DISSOCIATIVE RECOMBINATION OF MOLECULAR IONS

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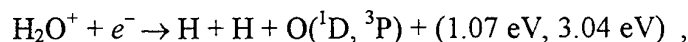
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Experiments in ion storage rings have shown that dissociative recombination of ions of type  $AH_2^+$  leads to three-body breakup in about two thirds of the events.<sup>1</sup> This is significantly more fragmentation than previously has been assumed in chemical modelling of interstellar molecular clouds.

Whereas measurements of branching ratios provide valuable data for chemical modelling, they do not shed light on the dynamics of the process. In order to provide insight of the recombination process, particle-imaging techniques have been applied at ion storage rings. CRYRING at the Manne Siegbahn Laboratory has been used to study<sup>2,3</sup>



where 1.07 eV refers to the kinetic energy release when oxygen occupies the  $^1D$  state and 3.04 eV is the same quantity when oxygen occupies the  $^3P$  state.

One can show that if the two O–H bonds break exactly simultaneous, and the  $H_2O^+$  bond angle is preserved, each H-atom would carry 1.46 eV and the  $O(^3P)$ -atom 0.12 eV. If, on the other hand, the breakup into three particles occurs in a sequence where one H-atom leaves an highly excited OH molecule, and the OH molecule dissociates when the first H-atom is already far away, the H-atom sharing of kinetic energy would be roughly 90% and 10% of the available energy. The experimental data is best fitted by the assumption that the kinetic energy is randomly shared between the H-atoms. The data also show that the bond angle is not preserved when  $O(^3P)$  is formed, while the opposite is true for  $O(^1D)$  production. The  $O(^3P):O(^1D)$  branching ratio was found to be  $(3.5 \pm 1):1$

Experiments at CRYRING have also been performed with  $NH_2^+$ ,  $CH_2^+$ ,  $H_3^{+4}$  and  $H_2D^+$ .<sup>4</sup>

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**Photoelectron-Photofragment Coincidence Studies of the  
Energetics and Dynamics of Alkoxy Radicals**

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Photoelectron-photofragment coincidence techniques provide a new approach to the study of alkoxides and alkoxy radicals. Photodetachment of both cyclic and linear alkoxides in the visible and near UV has been shown to yield both stable radicals and dissociative neutral products. Photoelectron-photofragment coincidence experiments provide insights into not only the electron affinities and structure of the neutral species, but also the dissociation pathways and dynamics. In the case of the strained ring compounds, including cyclopropoxy, cyclobutoxy and the cyclopentoxy radical, interesting effects arising from the conjugation of the O atom lone pair and radical orbitals with the ring orbitals are observed. We have also studied the photodetachment processes of 2-propyn-1-oxide ( $\text{HCCCH}_2\text{O}^\bullet$ ), formed by proton abstraction from propargyl alcohol. This species only yields stable products upon photodetachment, but shows a large splitting in the two lowest electronic states of the neutral owing to the interaction of the O atom orbitals with the carbon-carbon triple bond. Our new ability to carry out photodetachment imaging allows sensitive detection of near zero electron kinetic energy features, in principle allowing us to extend these measurements to much higher resolution by implementing tunable laser photodetachment in the near future.

This work was supported by the National Science Foundation and the US Department of Energy

## Photodissociation of the free radicals HNCN and HCNN

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The photodissociation spectroscopy and dynamics of the free radicals HNCN and HCNN are investigated using fast radical beam photodissociation spectroscopy. In these experiments, the precursor anion ( $\text{HNCN}^-$  or  $\text{HCNN}^-$ ) is generated, mass-selected, and photodetached. The resulting radicals are then photodissociated, and both photofragment yield spectra and kinetic energy/angular distributions are measured. Both radicals dissociate exclusively to  $\text{CH} + \text{N}_2$ ; the nearly isoenergetic but spin-forbidden channel  $\text{N}(^4\text{S}) + \text{HCN}$  is not observed. The dissociation mechanisms of the two radicals are very different. HNCN undergoes internal conversion to its electronic ground state and then dissociates through a cyclic transition state, whereas HCNN primarily undergoes simple bond fission. The relation between these results and the mechanism of the  $\text{CH} + \text{N}_2$  reaction will be discussed.



## LASER SPECTROSCOPY OF FREE RADICALS IN HYDROCARBON OXIDATION

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The oxidation of hydrocarbons is a complex process proceeding along many pathways involving numerous reactive intermediates. Under moderately low temperature conditions, the hydrocarbon radicals initially formed by H abstraction, react rapidly with  $O_2$  to form peroxy radicals,  $RO_2\cdot$ . Alkoxy radicals,  $RO\cdot$ , can result from the reactions of  $RO_2\cdot$  with itself and with odd oxygen species, e.g., O and NO, as well as other reactions. Such radicals play key roles in the branching reactions of low temperature combustion processes. They are also critical to the understanding of atmospheric chemistry because of their participation in the ozone and  $NO_x$  cycles, as well as smog chemistry.

The spectroscopy of peroxy radicals is sparse indeed. Most studies have focussed upon a broad ( $\approx 40$  nm) unstructured absorption around 240 nm. While strong and easily accessible, this absorption provides no structural information about the peroxy radicals and rarely even allows the distinction of one peroxy radical  $RO_2\cdot$  from another  $R'O_2\cdot$ .

The peroxy radicals also have an  $\tilde{A}-\tilde{X}$  band (origin  $\approx 6000-8000\text{ cm}^{-1}$ ) which is much weaker and historically hard to access. However it should provide structured spectra that easily distinguish among the various peroxy radicals. We have developed a cavity ring-down spectroscopy (CRDS) apparatus to obtain good quality IR spectra, with some rotational resolution under ambient temperature conditions, for several peroxy radicals including methyl, ethyl, isopropyl and t-butyl peroxy. In addition we have observed some fluorinated peroxy radical spectra. The talk will discuss both the CRDS spectra and the possible applications to the study of peroxy radical reactions.

By contrast the laser induced fluorescence (LIF) spectra of the smaller alkoxy radicals (methoxy, ethoxy, etc.) is quite developed. It is based upon their well-known near-UV transition. The LIF spectra of larger alkoxy radicals would be valuable because of the radicals' presence in combustion mechanisms for common fuels such as gasoline. However, conventional wisdom dictates that quantum yields for fluorescence would likely decrease rapidly for the larger species, and, in any case, any spectra resulting from these radicals would likely be quite congested revealing little information.

Somewhat surprisingly, we have recently obtained good LIF spectra for over 20 alkoxy radicals,  $C_nH_{2n+1}O\cdot$ , with  $n \leq 12$  carbon atoms. We will discuss the tendency of the electronic origins of these bands to fall into distinct families, based upon the branching of the hydrocarbon chain. In the spectra of the larger alkoxy radicals a small number of vibrational excitations appear to persist. There is also evidence for more than one conformer in the jet spectra.

Rotationally resolved LIF spectra have now been obtained for a number of jet-cooled  $RO\cdot$  radicals. The analysis of these spectra will be discussed with particular emphases upon determining which conformers are the carriers. The importance of these conformers for different oxidation mechanisms will be discussed.

## Stereodynamics of OH

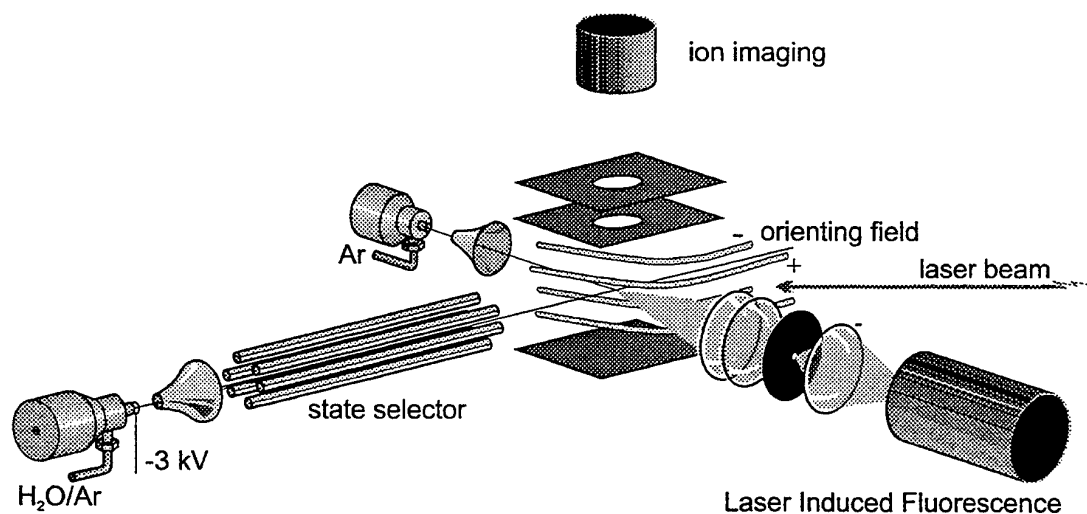
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The outcome of a collision of two molecules is not only determined by the intermolecular potential and the collision energy but also by the relative orientation of the two molecules. Whereas a specific relative orientation may lead to a chemical reaction the same reaction may be prohibited when the molecules are oriented in the opposite direction. Thus far, collision studies are generally performed with non-oriented molecules and steric effects stay concealed. In recent crossed molecular beam studies on OH we observed dramatic effects of the relative orientation. In OH-Ar scattering even differences between O-side and H-side collisions of up to an order of magnitude were measured. These differences are not caused by kinetic effects only; the open electronic shell structure of OH and the OH-Ar potential energy surface have to be taken into account to explain the observed inelastic effects. The measurement of orientation effects provides a unique tool to determine the anisotropy of the potential energy surface.

The choice for OH is based not only on its relevance in many different physical and chemical processes but also on the fact that this molecule is a nearly ideal molecule to study orientation effects in state resolved collision studies. The molecule is very asymmetric, the obtainable degree of orientation is the highest one reported thus far, and the OH molecules can be produced in a single rotational energy state, allowing detailed state resolved measurements.

Orientation effects have been studied for elastic and inelastic collisions of OH radicals in a crossed beam experiment. The OH( $X^2\Pi$ ) radicals were prepared in the upper  $J=3/2$   $\Lambda$ -doublet state by hexapole state selection and oriented with their O- or H-end towards the collision partner by a static electric field in the collision zone. In the collision area an OH density of about  $10^{11}$  molecules/cm<sup>3</sup> in the upper  $\Lambda$ -doublet state is obtained. The direction of the electric field is parallel to the relative velocity. Reversing the electric field direction switches the orientation of the OH molecules relative to the secondary molecules, which enables a quick and direct measurement of the effect of O-side versus H-side collisions. The degree of orientation has been determined by high resolution LIF spectroscopy on the Stark splittings in the orientation field. State resolved detection takes place by either laser induced fluorescence (LIF), such as in case of OH, or resonantly enhanced ionisation, which is applied to HCl or CO. Measurements are performed on the internal energy distribution of the scattered molecules and reaction products as a function of collision energy at different OH orientations. Cross sections down to  $0.1 \text{ \AA}^2$  can be detected. Detailed information about the experimental set up can be found in ref. 1 and 2.



View of the crossed pulsed molecular beam setup with electrostatic state selector, orientation field, LIF detection and ion imaging.

Steric asymmetry factors have been determined for rotational excitation up to the  $\Omega=3/2$ ,  $J=9/2$  and  $\Omega=1/2$ ,  $J=5/2$  state. In collisions with Ar differences up to a factor 8 in cross section were found between O-end and H-end impact [1]. In general a slight preference for O-end impact was found for low rotational excitation, while a strong preference for H-end impact was measured for excitation to high rotational states. The experimental results are compared to quantum scattering calculations on *ab initio* potential energy surfaces developed by Degli Esposti and Werner [3] and recently by Klos *et al.* [4]. The agreement between experiment and calculations based on the Klos and Chalasinski potential is excellent for transitions to states of  $A''$  symmetry and good for transitions to states of  $A'$  symmetry. Also results of measurements on  $M_J$  substate changing collisions in rotationally elastic scattering of OH by Ar will be discussed [5].

In addition orientation effects measured for collisions of OH by other molecules will be presented. In inelastic scattering of OH by CO indications for the occurrence of the HOCO collision complex were obtained for the situation where the O side is directed towards the CO molecule [6]. We also hope to present the results of present measurements on scattering by HCl. We expect to see indications that a reaction resulting in  $\text{H}_2\text{O} + \text{Cl}$  is preferred above inelastic excitation if the O-side is pointing towards HCl, whereas the reverse situation may occur for the opposite orientation. Preparations are being made to observe the reaction fragments by resonant ionisation detection.

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Theoretical studies of electronically non-adiabatic effects in reactions of  
halogens:  $F + HD \rightarrow HF + D$  and  $Cl + H_2 \rightarrow HCl + H$

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In chemical reactions nonadiabaticity occurs when the reacting atoms move on more than one potential energy surface. Because of their experimental accessibility, the reactions of  $H_2$  with halogens are paradigms for exothermic triatomic reactions. The open-shell character of a halogen atom in its ground electronic state ( $^2P$ ) raises two important questions: (1) what is the reactivity of the excited ( $^2P_{1/2}$ ) spin-orbit state and (2) how well will the dynamics of the reaction be described by calculations on a single potential energy surface (PES).

We have recently developed the formalism for full quantum scattering studies of halogen- $H_2$  reactions including all three relevant PESs and all spin-orbit and coriolis coupling terms.

Using this formalism, we will describe calculations of product translational and internal energy distributions in the  $F+H_2(HD) \rightarrow HF + H(D)$  reaction. In addition, we will present calculations of the relative reactivity of ground and spin-orbit excited Cl in reaction with  $H_2$ . The quantum scattering calculations are based on sophisticated multi-reference *ab initio* PESs including the determination of the spin-orbit coupling as a function of geometry. The focus of these calculations will be the investigation of the importance of nonadiabatic transitions in the entrance channel.

We shall use our theoretical studies to investigate critically recent experimental work from the groups of Liu (Taiwan) and Nesbitt (Boulder), which probe the reactivity of the excited spin-orbit state.

## Vibrational State Resolved Studies of Reactive and Inelastic Collision Dynamics

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Crossed molecular beams experiments with vibrational state resolution have been performed on the simplest four-atom reaction,  $\text{OH} + \text{D}_2 \rightarrow \text{HOD} + \text{D}$ . In good agreement with the most recent quantum scattering predictions, mode specific reaction dynamics is observed, with vibration in the newly-formed OD bond preferentially excited to  $v = 2$ . Good agreement was observed between the experimentally-measured HOD vibrational distributions and those predicted theoretically. This demonstrates that quantum theoretical calculations, which in the past decade have achieved remarkable accuracy for three-atom reactions involving three dimensions, have progressed to the point where it is now possible to accurately predict energy disposal in 4-atom reactions involving six dimensions. We are presently studying the reaction  $\text{OH} + \text{D}_2 (v=1) \rightarrow \text{HOD} + \text{D}$  at collision energies below threshold for reaction of  $\text{D}_2 (v=0)$ . Recent progress on this system will be discussed.

Vibrationally inelastic scattering of Rydberg H atoms from  $\text{N}_2$  and  $\text{O}_2$  has been studied using the H atom Rydberg time of flight method. In this experiment, a photolytic H atom beam is crossed with a molecular beam. On average, four times more vibrational excitation was observed in collisions with  $\text{O}_2$  than with  $\text{N}_2$ . This behavior is quite similar to that seen previously in proton scattering experiments. Vibrational excitation of  $\text{O}_2$  results from collisions in which an electron is briefly transferred from  $\text{O}_2$  to the proton core, while the Rydberg electron remains a spectator. This provides further evidence that the free electron model, often applied to collisions involving the Rydberg electron, may be applied to collisions involving the ionic core leading to substantial momentum transfer.

## Free radicals, short-lived compounds, and their impact on the Earth's atmosphere

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The lifetime of a chemical compound introduced into the atmosphere depends on its reactivity with free radicals, its photolysis rate, and its rate of loss via heterogeneous and multiphase reactions. Therefore, these processes are studied in the laboratory to determine the lifetimes of chemical species. Transport of species from the troposphere to the stratosphere is the main pathway for the delivery of chemically active species to this region. It is assumed that the short-lived compounds, either emitted at the Earth's surface (due to natural and anthropogenic processes) or produced via chemical degradation, would be removed in the troposphere and would not be transported into the stratosphere. Therefore, one of the strategies that has been employed to reduce the delivery of anthropogenic species into the stratosphere has been to design molecules that are short-lived in the troposphere. Here, I will explore the possibility that a short-lived compound is degraded in the troposphere to yield sufficiently long-lived chemicals that may yet transport the element of interest (e.g., halogens and sulfur) to the stratosphere.

Anthropogenic chlorine compounds are now known to be the primary reason for stratospheric ozone depletion. Chloral, a compound produced in the degradation of methyl chloroform in the troposphere, was usually considered to be an insignificant source of chlorine to the stratosphere. Studied in our laboratory suggests that chloral degrades in the troposphere to yield phosgene, which may still get to the stratosphere. I will describe the kinetics and photochemical studies on chloral that led to this suggestion.

Bromine is known to be much more potent than chlorine in destroying stratospheric ozone. Therefore, very short-lived bromine compounds have been proposed as replacements for longer-lived bromine compounds. One such example is n-bromopropane. The key to determining if bromine in this compound will get to the stratosphere is to elucidate the site specific H atom abstraction by OH; different sites yield different end products. I will describe our efforts to obtain site-specific reactivity of OH with n-bromopropane and the chemistry of bromoacetone that may be produced.

Short-lived natural emissions may also lead to longer-lived compounds. One example is the possibility that short-lived sulfur containing compounds such, as  $\text{H}_2\text{S}$  and  $\text{CH}_3\text{SCH}_3$ , are converted to very long-lived OCS. I will described our studies on these system to evaluate the possible production of OCS in the degradation of sulfur compounds.

All these discussions will be based on laboratory studies of the kinetics of free radicals in our laboratory.

## Intermediates in proton transfer and nucleophilic bimolecular substitution (S<sub>N</sub>2) reactions: a theoretical study

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Several proton-bound ionic complexes, which may be considered as intermediates in proton transfer reactions, have been studied theoretically. Among them are complexes of a rare-gas atom (Ar-Xe) with the cations HCO<sup>+</sup>, HN<sub>2</sub><sup>+</sup> and HNCH<sup>+</sup>. Various spectroscopic properties are calculated in all cases. The proton stretching vibration of (N<sub>2</sub>)H<sup>+</sup>(N<sub>2</sub>) is predicted around 800 cm<sup>-1</sup>, with a large transition dipole moment of 1.15 D. Both (N<sub>2</sub>)H<sup>+</sup>(N<sub>2</sub>) and (HCN)H<sup>+</sup>(NCH) have linear centrosymmetric equilibrium structures while isoelectronic (OC)H<sup>+</sup>(CO) has two equivalent asymmetric energy minima which are separated by a small barrier of 382 cm<sup>-1</sup>. Furthermore, anionic complexes of type Hal<sup>-</sup> ... HCCH (Hal: F, Cl, Br and I) are studied in considerable detail. The complex formed between a fluoride anion and acetylene is most strongly bound and exhibits strongly anharmonic behaviour.

The potential energy surfaces for nucleophilic bimolecular substitution (S<sub>N</sub>2) reactions in the gas-phase are characterized by two rather deep wells in the entrance and exit channel. The examples Cl<sup>-</sup> + CH<sub>3</sub>Cl → CH<sub>3</sub>Cl + Cl<sup>-</sup> (1) and Cl<sup>-</sup> + CH<sub>3</sub>Br → CH<sub>3</sub>Cl + Br<sup>-</sup> (2), with either symmetric or asymmetric reaction profiles, are considered. In both cases, two-dimensional analytical potential energy functions were constructed on the basis of CCSD(T) calculations with large basis sets. In the quantum dynamics calculations, Radau coordinates were employed to describe the carbon-halogen stretching modes. Making use of the filter diagonalization method and an optical potential, bound states as well as resonance states have been calculated. For both reactions, the resonance widths fluctuate over several orders of magnitude. Strong symmetry specificity was found for reaction (1), with the lifetimes of the gerade states being shorter by about two order-of-magnitude compared to those of ungerade states in the same energy regime. An explanation is given in terms of an adiabatic model formulated in hyperspherical coordinates.

## **Production and Characterization of Open Shell Atom and Free Radical Beams: a Systematic Study of Intermolecular Forces from Scattering Experiments.**

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Intense and stable beams of open shell atoms and free radicals, emerging from microwave and radiofrequency discharge sources, have been characterized by magnetic analysis and subsequently employed in scattering experiments [1].

Data of beam transmittance across a Stern Gerlach magnet, measured at selected velocities as a function of the field strength, provide direct information on the sublevel distribution of the analyzed species and suggest a useful method to induce, in a controlled way, distribution changes in the transmitted beam.

Scattering experiments have been carried out on many systems. The investigation of an ample phenomenology permitted us to study and to model the intermolecular forces, leading to the formulation of new empirical and semiempirical methods useful for their calculations [2].

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## Ion Imaging study of the Inelastic Scattering of NO with Ar

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Inelastic scattering of a molecule with an atom reveals much about the intermolecular potential. In this study we study to scattering of the NO radical with Ar. We have measured the differential cross section, the alignment of the J vector of the NO and the orientation of the J vector. Ion imaging techniques allow us to determine these quantities for individual quantum states of the product. Each measurement reveals different information about the potential and the collision dynamics. The measurement of the differential cross section of a reaction for each product quantum state is sensitive to both the repulsive and attractive parts of the intermolecular potential. This quantity is a stringent test of *ab-initio* potential energy surfaces. The measurement of the alignment and orientation of the product angular momentum vector tell us about the collision dynamics.

## Free Radical Complexes in Helium Nanodroplets: High Resolution Infrared Spectroscopy

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Superfluid helium droplet spectroscopy (SHEDS) is providing new insights into a wide array of structural and dynamical processes, including superfluidity, solvent-solute interactions, rotational and vibrational dynamics, the formation of high spin species and the self assembly of novel new cluster structures. Infrared laser spectroscopy has proven to be particularly useful in these studies, due to the fact that the resolution of the associated spectra is often very high. For these studies, helium turns out to be a nearly ideal matrix for isolating molecules. These methods are now being used in our laboratory to study biomolecules, radicals, ions, hydrogen bonded complexes and metal nanoparticles.

The apparatus built at UNC uses a bolometer to measure the laser-induced change in the helium droplet beam energy. A color center laser operating in the range 2800 - 4500  $\text{cm}^{-1}$  is used to vibrationally excite the molecule in the droplet, which results in one of two outcomes. Vibrational quenching of the molecule by the helium results in the evaporation of several hundred helium atoms, thus reducing the energy delivered by the helium droplets to the bolometer.

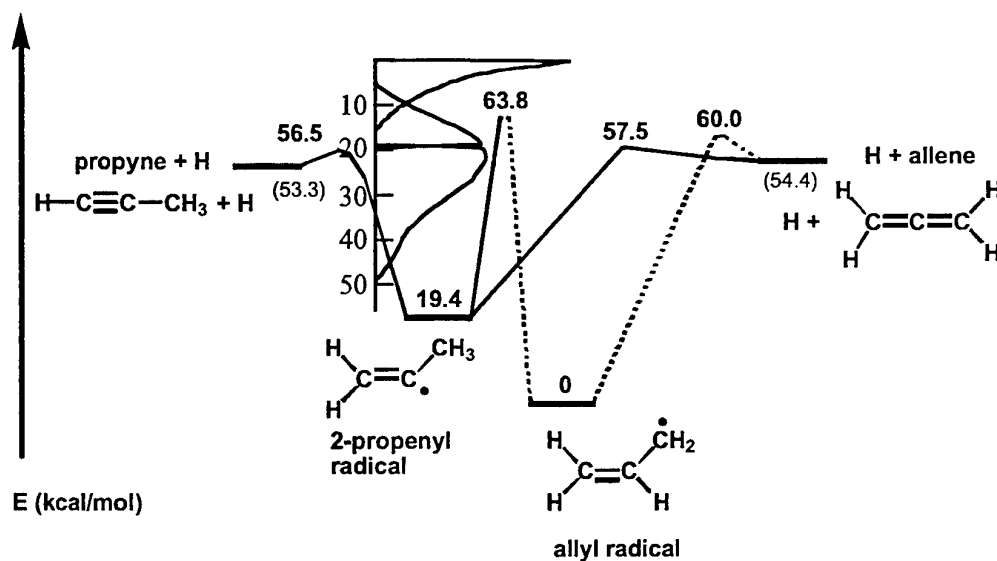
The focus of the present talk will be on the study of free radicals solvated in helium droplets. The radicals of interest are formed in the gas phase (by pyrolysis or microwave discharge) and then captured by the droplets for spectroscopic study. Radical complexes are also being studied, including such systems as Br-NCH. Rotational fine structure in the spectra of these complexes provides detailed structural information. The advantages of using helium droplets to stabilize pre-reactive complexes will be discussed and illustrated.

**Molecular beam studies of the competing bond fission channels  
of isomerically-selected radicals: allyl, 2-propenyl, and 1-propenyl radicals**

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New molecular beam scattering experiments investigate the internal energy dependence of the unimolecular dissociation and isomerization pathways of selected radical isomers under collision-less conditions. While complementary work in other groups has focused on the photodissociation pathways of radicals, this work seeks to probe the unimolecular reactions of radical isomers at lower internal energies where the branching between competing dissociation product channels is a sensitive function of internal energy.

The talk focuses on three specific  $C_3H_3$  radical isomers: allyl radical, 2-propenyl radical, and 1-propenyl radical. The work first resolves the dramatic discrepancy on the relative heights of the allyl→2-propenyl isomerization barrier and the barrier to the unimolecular dissociation to H + allene. Recent ab initio work suggested the isomerization barrier is about 15 kcal/mol higher than that determined from bulk kinetics measurements, putting it above instead of below the C-H bond fission barriers. It then measures the differing onsets of and the change in branching ratio between the H + allene versus the H + propyne product channels of the high-energy 2-propenyl isomer as a function of internal energy in the radical. In contrast, the allyl radical branches essentially exclusively to H + allene products at the internal energies probed. In the 1-propenyl radical a C-C fission product channel opens. For these electronically facile reactions, we compare the experimental results with the predictions of statistical transition state theories using a single potential energy surface calculated at the G3(B3LYP) level of theory. We end by discussing the extension of the work to more electronically complex systems.



## LASER STUDIES OF FREE RADICAL REACTIONS – FROM DIATOMICS TO DNA

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In recent years, a large number of linear and nonlinear laser-based diagnostic techniques for nonintrusive measurements of species concentrations with high temporal and spatial resolution were developed and have become extremely valuable tools to study many aspects of radical kinetics.

Reactions of translationally excited hydrogen atoms with  $D_2$ ,  $O_2$  and HCl at different center-of-mass energies have been studied under single collision conditions with the laser photolysis/laser induced fluorescence pump-probe technique. The experimental results are compared with results from recent quassiclassical and quantum scattering calculations on ab initio potential energy surfaces.

Nonlinear laser spectroscopic techniques using in-situ infrared-visible sum-frequency (SFG) generation can now bridge the pressure and materials gap to provide kinetic data for catalytic radical reactions. This is illustrated for reactions of CO and NO on single crystal and polycrystalline platinum surfaces in a stagnation flow arrangement.

Finally experiments on the kinetics of enzyme reactions using single DNA molecules in microcapillaries are presented. This could be achieved by the development of new dyes with functional groups for covalent coupling of biomolecules with nearly identical absorption and emission bands beyond 600 nm and high fluorescence quantum yields but with different fluorescence lifetimes. Single dye labelled nucleotid molecules can be distinguished after exonuclease clearance by recognition of the fluorescence lifetimes using a confocal microscope and pulsed semiconductor lasers.

## Barrierless Reactions: Radical Products and Radical Ideas

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Photoinitiated unimolecular decomposition via a barrierless pathway has been studied for the reaction  $\text{NO}_2 \rightarrow \text{O}(^3\text{P}_2) + \text{NO}(\text{X}^2\Pi_{1/2}, v=0)$  for  $0 \leq E - D_0 \leq 27 \text{ cm}^{-1}$ , by using expansion-cooled samples and the time-resolved pump-probe technique. To examine the threshold region with enough resolution to discern abrupt changes in the rate constant, should they occur, a pump-probe cross correlation temporal width of  $\sim 10 \text{ ps}$  and a pump linewidth  $\sim 3 \text{ cm}^{-1}$  has been used. The rate constant  $k(E)$  increases by an order of magnitude, from  $\sim 2 \times 10^{10} \text{ s}^{-1}$  to  $\sim 1.6 \times 10^{11} \text{ s}^{-1}$ , the latter being a lower bound imposed by the experimental arrangement.  $k(E)$  reflects the complex nature of the levels and the multiple potentials believed responsible for the high vibronic level density that has been observed just below  $D_0$ . These results bridge the gap between spectroscopic studies that have been carried out at energies just above  $D_0$  and the ultrafast experiments that have measured rate constants in this energy region with pump laser spectral widths of  $\sim 30 \text{ cm}^{-1}$ . Theoretical models will be discussed critically. It is known that the partitioning of a Hilbert space into two subspaces, *e.g.*, by using orthogonal projection operators, yields compact forms for effective Hamiltonians for each of the subspaces. When one (the  $Q$  space) contains the molecular bound states and the other (the  $P$  space) contains the dissociative continua, a simple form for the effective non-Hermitian  $Q$ -space Hamiltonian can be obtained, subject to reasonable approximations. Namely,  $H^{\text{eff}} = H^0 - i\tilde{\Gamma}/2$ , where  $H^0$  operates in the  $Q$  space and the width matrix  $\tilde{\Gamma}$  accounts for couplings of the  $Q$ -space levels to the  $P$ -space continua. This formalism has failed to model satisfactorily the statistical transition state theory (TST) of unimolecular decomposition in the regime of overlapping resonances, where nearly all such reactions occur. By manipulating a simple model problem, for which exact solutions are obtained, into the form  $H^0 - i\tilde{\Gamma}/2$ , it is shown that the independent open channels in the random matrix  $H^{\text{eff}}$  model are inconsistent with TST. Rather, this model is one of *gateway states*, *i.e.*, bound states that are coupled to their respective continua and to a manifold of zeroth-order bound states, none of which are coupled directly to the continua. Such models (which are based on the partitioning of the Hilbert space into just two subspaces) are flawed as TST models of unimolecular decomposition in several respects, including complete breakdown in the regime of strongly-overlapping resonances, as manifest in bifurcations of the distributions of resonance widths. A simple model is presented that accounts for quantum fluctuation phenomena and has no bifurcation problems.

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## High resolution IR laser studies of radicals: Spectroscopy and reaction dynamics

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Shot noise limited direct absorption with tunable near IR lasers provides an extremely sensitive and nearly universally applicable method for spectroscopic and dynamic studies of radicals. This talk will address two applications of such near infrared methods in our group. i) Novel pulsed discharges have been combined with slit supersonic expansions to obtain unusually intense sources (up to  $10^{15}$  #/cm<sup>3</sup>) of jet cooled (10 K) molecular radicals under long path length conditions ideal for detection via high resolution absorption. Spectroscopic results will be presented for important combustion species (e.g. methyl, ethyl, allyl, cyclopropyl) which elucidate the importance of large amplitude vibrational dynamics even in "simple" hydrocarbon radicals. ii) High sensitivity direct IR laser absorption in crossed supersonic jets is used to investigate state-to-state dynamics of F atom abstraction reactions under single collision conditions. Applications to sample atom + diatom (e.g. F + HD) and atom + polyatom (e.g. F + H<sub>2</sub>O) systems will be used to illustrate the method, and which in the case of F + HD provide state-resolved evidence for quantum resonance behavior due to quasibound H atom chattering between F and D atoms near the transition state region.

## Studying Reaction Intermediates and Reaction Dynamics/Kinetics with Time-Resolved Fourier-Transform Spectroscopy

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Following photodissociation of vinyl halides ( $\text{CH}_2\text{CHX}$ ,  $\text{X} = \text{F}$ ,  $\text{Cl}$ , and  $\text{Br}$ ) at 193 nm, spectrally resolved vibration-rotational infrared emission spectra of  $\text{HX}$  are detected with a step-scan Fourier-transform spectrometer. Emission from  $\text{HX}$  up to  $v = 7$  showing bimodal rotational distributions is observed. The low- $J$  and high- $J$  components correspond to four-center and three-center  $\text{HX}$ -elimination channels of vinyl halides, respectively. An impulse model predicts little rotational excitation but a lot of vibrational excitation for four-center elimination and extensive rotational excitation for three-center elimination. It also explains satisfactorily why the rotational energy of  $\text{HF}$  produced via three-center elimination of  $\text{CH}_2\text{CHF}$  is smaller than that of  $\text{HCl}$  or  $\text{HBr}$  produced from a similar channel. Observed branching ratios are consistent with those predicted based on RRKM theory. Similar experiments were performed for  $\text{CF}_2\text{CHCl}$ .  $\text{HF}$  ( $v < 5$ ) with small rotational excitation and highly rotational excited  $\text{HCl}$  ( $v < 3$ ) were observed, consistent with our model predicting formation of  $\text{HF}$  and  $\text{HCl}$  from four-center and three-center elimination, respectively.

Time-resolved absorption of vibrationally excited  $\text{CH}_4$  ( $v_2=1$  or  $v_4=1$ , designated as  $\text{CH}_4(v^*)$ ) was observed after laser irradiation of a flowing mixture containing  $\text{Cl}_2$ ,  $\text{CH}_4$ , and  $\text{Ar}$  at 355 nm in a multipass absorption cell. Experimental evidence indicates that the reaction  $\text{Cl} + \text{CH}_4$  is rate-determining to formation of  $\text{CH}_4(v^*)$ ;  $\text{CH}_4(v^*)$  is likely produced through energy transfer from vibrationally excited  $\text{CH}_3\text{Cl}$  that is produced via secondary reactions. Formation of  $\sim 1\%$   $\text{CH}_4(v^*)$  after laser photolysis can thus explain why rate coefficients determined previously through flash photolysis near 220K are  $\sim 20\%$  greater than those determined in a discharge-flow system because the rate coefficient for the reaction  $\text{Cl} + \text{CH}_4(v^*)$  is much greater than that for  $\text{Cl} + \text{CH}_4$ , especially at lower temperatures.

We also applied time-resolved detection in absorption mode to detect reaction intermediates such as  $\text{ClCO}$  (from  $\text{Cl} + \text{CO}$ ),  $\text{ClC}_2\text{H}_2$  (from  $\text{Cl} + \text{C}_2\text{H}_2$ ), and *cis*- $\text{HOCO}$  (from  $\text{Cl} + \text{HCOOH}$ ); preliminary results will be presented.

**ABSTRACTS  
OF  
CONTRIBUTED PAPERS**

*Hot Topics*



## UV and Near-UV Photodissociation Dynamics of Small Hydrocarbon Free Radicals

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Photodissociation dynamics of jet-cooled vinyl radical ( $C_2H_3$ ) has been investigated by using the high- $n$  Rydberg H-atom time-of-flight technique at near-UV (327.4 and 366.2 nm) and UV (240 nm) photolysis wavelengths. For near-UV photodissociation of  $C_2H_3$  via the first excited  $\tilde{A}^2A''$  state, ground state ( $\tilde{X}^1\Sigma_g^+$ ) acetylene and H atom products are identified. Product center-of-mass (c.m.) translational energy distributions reveal two well-resolved, highly-inverted vibrational progressions of the  $C_2H_2(\tilde{X}^1\Sigma_g^+)$  product (most likely  $C\equiv C$  stretch and its combination band with C-H bend, with the  $C\equiv C$  stretch quanta up to 7). Anisotropic H-atom angular distributions are observed, indicating a short  $\tilde{A}^2A''$  state lifetime with respect to dissociation. Furthermore, the  $C\equiv C$  stretch and the  $C\equiv C$  stretch with a C-H bending vibrational progressions have different anisotropy parameters ( $\beta = 0.8 \pm 0.3$  and  $-0.7 \pm 0.2$ , respectively), suggesting two dissociation pathways in the  $HCCH + H$  channel. At the UV photolysis wavelength near 240 nm, where the second and third electronically excited states of  $C_2H_3$  are accessible, the same two highly-inverted vibrational progressions of acetylene are observed. In addition, an isotropic, broad, and structureless feature is identified in the slow portion of the c.m. product translational energy distribution, suggesting the  $H_2CC + H$  channel or another highly excited acetylene product channel. Photodissociation of the  $C_2D_3$  radical has been examined at 240 nm as well, and its dynamic information is similar to that of  $C_2H_3$ .

UV photodissociation of jet-cooled ethyl radical ( $C_2H_5$ ) has also been studied. Upon excitation into the  $\tilde{A}^2A_1(3s)$  state by 245-nm UV radiation, ethyl dissociates into H atom and ethylene. Bimodal profile in the c.m. translational energy distribution of the products, as well as the energy-dependent product angular distribution, suggests two different dissociation pathways. A slow [with  $\langle E_T \rangle \sim 0.35E_{avail}$ ] and isotropic component corresponds to unimolecular dissociation of the radical, presumably after internal conversion from the  $\tilde{A}$  state to the ground state of ethyl. A previously unobserved fast [with  $\langle E_T \rangle \sim 0.78E_{avail}$ ] and anisotropic ( $\beta = 0.5 \pm 0.1$ ) component corresponds to a direct, rapid H-atom scission via a nonclassical H-bridged transition state from the  $3s$  state to yield  $H + C_2H_4(\tilde{X}^1A_g)$ . Site-selective loss of the  $\beta$  hydrogen atom is confirmed by using the partially-deuterated  $CH_3CD_2$  radical.

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# Fourier Transform Microwave Spectroscopy of the Acetyl Radical

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The acetyl radical has been known as an important intermediate in many organic chemical reactions. However, presumably because of its chemically fragile character, almost no detailed spectroscopic studies have been reported, preventing us from monitoring this transient species by spectroscopic methods in real time and thus from elucidating the mechanism of many reactions that are central to chemistry. Endo and Hirota thus started searching for rotational spectra of acetyl by using direct absorption millimeter-wave spectroscopy. Although they succeeded in recording three successive rotational transitions of  $N = 6 \leftarrow 5$ ,  $7 \leftarrow 6$  and  $8 \leftarrow 7$ , all of these transitions were found to consist of too many lines, making the assignment extremely difficult. Later Endo and his collaborators set up a Fourier transform spectrometer and observed the lowest  $N$  transition:  $1_{01} \leftarrow 0_{00}$ ; this transition appeared separated in two groups of lines, the higher-frequency one being reasonably assigned to A and the lower-frequency one to E sub-state of  $\text{CH}_3$  internal rotation. Although the A lines were fit to a spectral pattern expected for a doublet asymmetric rotor, it took us some time to understand the E lines. We needed at least two parameters for each of Fermi and dipole-dipole hyperfine interactions. We have then extended the observation to the  $N = 2 \leftarrow 1$  transitions. Unfortunately the sensitivity of our spectrometer is not sufficient enough for detecting weak fine and hyperfine components of this rotational transition, and hence the spectral assignment is still not finalized, especially for those lines associated with  $K_a = 1$ . Nevertheless, we have derived most of the important molecular parameters by a simultaneous analysis of the A:  $N = 1 \leftarrow 0$ ,  $2 \leftarrow 1$ ,  $K_a = 0$ , E:  $N = 1 \leftarrow 0$ , as listed below. The potential barrier  $V_3$  for methyl internal rotation was about  $140 \text{ cm}^{-1}$ .

## Molecular Constants of Acetyl derived from

A:  $N = 1 \leftarrow 0$ ,  $2 \leftarrow 1$ ,  $K_a = 0$ , E:  $N = 1 \leftarrow 0$  Transitions (in MHz)

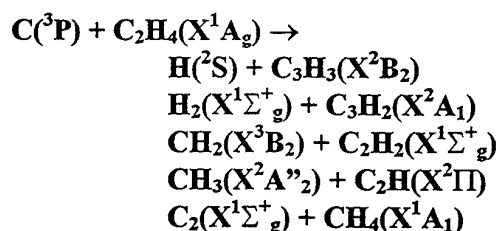
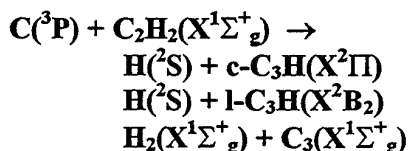
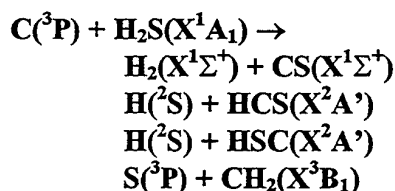
$(B + C)/2$	9774.7307 (14)	$b_A$	9.4810(16)
$\Delta_N$	0.00659(19)	$b_E$	9.5981(39)
		$b_{EE}$	-17.8218(21)
$\epsilon_{aa}$	616.25(83)		
$(\epsilon_{bb} + \epsilon_{cc})/2$	-13.1671(30)	$T_A$	2.8717(14)
$(\epsilon_{bb} - \epsilon_{cc})/2$	26.58(72)	$T_E$	2.7015(48)
$(\epsilon_{ab} + \epsilon_{ba})/2$	-69.13(13)	$T_{EE}$	0.4886(21)

**Fast-Flow Studies of the C + H<sub>2</sub>S, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> Reactions :  
A Comparison between Experimental and Theoretical Determinations of  
Atomic Hydrogen Production.**

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Atomic carbon is an important reactive species whose relevance ranges from combustion and hydrocarbon synthesis to interstellar chemistry. Despite their fundamental and practical importance, the major problem is that these reactions have several exoergic product channels which are not been clearly identified, owing to the difficulty in obtaining clean sources of atoms. In a flow system, the stripping of halogen atoms in CBr<sub>4</sub> by atomic potassium provided a clean source of carbon atoms. The following reactions, without barrier, were studied:



The experiments have been performed at room temperature, in He as carrier gas and at a total pressure of 1–2 Torr. The overall rate constants and the relative branching between channels yielding hydrogen atoms of these reactions have been determined from the VUV resonance fluorescence of the atoms.

Ab initio studies of the different stationary points of the C + H<sub>2</sub>S reaction have been performed. RRKM calculations have completed the overview of the absolute branching ratios. Previous theoretical studies performed on the C + C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> reactions, in agreement with our experimental results, underlined the role of the inter-system-crossing occurrence between triplet and singlet potential energy surfaces.

Recent studies on the kinetics at room temperature and down to 15 K, and on the dynamics using crossed molecular beam scattering technique, are noted.

Detailed SACM modeling of the reactions  $\text{O} + \text{OH} \rightleftharpoons \text{O}_2 + \text{H}$  and  
 $\text{O} + \text{OD} \rightleftharpoons \text{O}_2 + \text{D}$  at  $0 \leq T \leq 300 \text{ K}$

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The reaction  $\text{O} + \text{OH} \rightarrow \text{H} + \text{O}_2$  is both of astrochemical and atmospheric importance. At the same time, the reverse reaction  $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$  is the dominant chain branching process in many combustion systems. Therefore, it has found great attention over many years. For the combined forward and backward reaction now experimental results from 150 to 5300 K are available. A series of new developments now provide the basis for a quantitative theoretical characterisation: the heat of formation of OH has been revised, the potential has been calculated more systematically by precise ab initio techniques, classical trajectory calculations have been made accounting for zeropoint energy constraints, adiabatic channel (SACM) calculations show that trajectory calculations are inappropriate for  $T \leq 300 \text{ K}$ , the lowest adiabatic channels have been elaborated indicating that quantum SACM rates exceed trajectory results by factors of about 3 at 10 K and 2 at 50 K. The present contribution reports on extended SACM calculations accounting for coupling of several types of angular momenta such as this is common in open electronic shell radical-radical reactions. In particular, it investigates kinetic isotope effects for H and D in this reaction under low temperature quantum conditions. Agreement between experiment and theory now seems to approach the 10 % range.

## Infrared Frequency-Modulation Probing of Product Formation in Reactions of Alkyl Radicals with O<sub>2</sub>

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Reactions of alkyl radicals with O<sub>2</sub> are important in understanding autoignition, engine knock, and pre-ignition chemistry. The R + O<sub>2</sub> reactions take place via initial formation of an excited alkylperoxy radical (RO<sub>2</sub>), which then can be collisionally stabilized or dissociate to reactants or to products. One possible fate of RO<sub>2</sub> is rearrangement to a hydroperoxyalkyl radical QOOH, which can then decompose to QO + OH or to Q + HO<sub>2</sub>. The QOOH species formed by this isomerization is also an intermediate in many models of hydrocarbon oxidation. Present understanding of these reactions is that HO<sub>2</sub> formation proceeds principally via concerted elimination from RO<sub>2</sub> which competes with the isomerization to form QOOH. The mechanism of R + O<sub>2</sub> reactions have been investigated by measuring the time-resolved production of HO<sub>2</sub> in Cl-initiated oxidation reactions. The oxidation of ethane, propane, cyclopentane, *i*-butane, and *n*-butane have been studied using CW infrared frequency modulation spectroscopy between 298 and 700 K following pulsed photolysis of Cl<sub>2</sub>. The yield of HO<sub>2</sub> is determined relative to the Cl<sub>2</sub>/CH<sub>3</sub>OH/O<sub>2</sub> system. The branching fraction to HO<sub>2</sub> + alkene in these R + O<sub>2</sub> reactions displays a dramatic rise with increasing temperature between about 550 K and 700 K (the "transition region") which is accompanied by a qualitative change in the time behavior of the HO<sub>2</sub> production. At low temperatures the HO<sub>2</sub> is formed promptly; a second, slower production of HO<sub>2</sub> is responsible for the bulk of the increased yield in the transition temperature region. The slower HO<sub>2</sub> production in the Cl-initiated alkane oxidation reactions display similar apparent activation energies, suggesting that the energetics of the HO<sub>2</sub> elimination transition state are similar for a broad range of R + O<sub>2</sub> systems. The experimentally observed HO<sub>2</sub> production is explained in the framework of recent *ab initio* and master equation calculations.

This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the U. S. Department of Energy

LABORATORY AND RADIO-ASTRONOMICAL SPECTROSCOPY OF THE HYPERFINE  
STRUCTURE OF  $\text{N}_2\text{D}^+$

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The millimeter- and submillimeter-wave spectrum of the  $\text{N}_2\text{D}^+$  molecular ion has been recorded by using a double-pass negative glow discharge cell, thus avoiding the Doppler shift which may affect the accuracy of transition frequency measurements.

The hyperfine structure of the  $J = 1-0$  transition due to the quadrupole coupling of both nitrogen nuclei has been resolved in laboratory and by radio astronomy at Nobeyama Radio Observatory, where this transition has been observed toward the quiescent low-mass cloud core L1512 in Taurus.

Improved spectroscopic constants and hyperfine parameters will be reported.

Photoinitiated Dissociation and Isomerization of the Hydroxymethyl Radical

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The chemistry of hydroxyalkyl radicals is important in atmospheric and combustion environments, since cleavage of the C-H bond is implicated in the reactions of several atoms and radicals with alcohols and alkanes. In particular, the methoxy  $\leftrightarrow$  hydroxymethyl system affords many opportunities to study both isomerization and dissociation on the ground potential energy surface. High vibrational levels of the ground electronic state of  $\text{CH}_2\text{OH}$  can be accessed in several ways: (i) by using internal conversion from excited electronic state, such as the  $3s(^2A')$  and the  $3p_z(^2A'')$  Rydberg states; and (ii) via direct vibrational excitation of  $\text{CH}_2\text{OH}$  accessed by pumping OH overtones as "bright" states. In the former method, levels that are  $\sim 3-4$  eV above the  $\text{H} + \text{CH}_2\text{O}$  asymptote are reached. In the latter – the region of the isomerization barrier is gradually approached from below.

The  $\text{D} + \text{CH}_2\text{O}(S_0)$  channel is a major pathway in the dissociation of  $\text{CH}_2\text{OD}$  excited to the origin band of the  $2A''(3p_z)$  Rydberg state. The mechanism involves predissociation, and the dissociation lifetime is on the order of a picosecond. The D photofragment was examined following origin band excitation using the "core sampling" variant of time-of-flight (TOF) spectroscopy. Both the kinetic energy release and the effective recoil anisotropy parameter,  $\beta_{\text{eff}}$ , were determined. The product kinetic energy distribution (KED) is broad, indicating that the formaldehyde co-fragment is in the ground electronic state but its internal energy extended to the thermochemical limit. The recoil anisotropy parameter  $\beta$  corresponds to fast ( $< 1$  ps) dissociation. We detect H and D signals correlated with REMPI in both  $\text{CH}_2\text{OD}$  and  $\text{CD}_2\text{OH}$  dissociation. The KED's corresponding to the H and D fragments are very different for the two isotopomers of  $\text{CH}_2\text{OH}$ . Whereas the D and H signals from  $\text{CH}_2\text{OD}$  and  $\text{CD}_2\text{OH}$ , respectively, are broad and extend to  $\sim 4$  eV, the corresponding H and D signals are much narrower, terminating at 1.5-2.0 eV. Thus, there are at least two different pathways leading to H and D. We have also started to examine how the dissociation mechanism is affected by exciting peaks other than the origin band of the  $3p_z(A'') \leftrightarrow \tilde{X}^2A''$  transition. With  $\text{CH}_2\text{OD}$ , we have obtained D photofragment yield spectra and KED's between 245 and 225 nm, and found that as the energy above the origin band increases, a *slow* component in the D speed distribution starts to grow in, whose relative importance increases with increasing excitation energy.

Recently, we also were able to assign the spectroscopy of the  $3s(A') \leftrightarrow \tilde{X}^2A''$  transition, and examine its couplings to the ground electronic state. The results of these studies will be reported as well.

## Inner-shell studies of free radicals and transient species by Synchrotron radiation

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Third generation SR undulator beam lines allow low density and highly reactive species to be studied in the gas phase using high photon energy resolution. Core-excited states in the OH and OD free radicals and the CS transient molecule have been investigated for the first time. In the case of the lowest O 1s excited state ( $^2\Sigma^+$ ) of OH and OD, vibronic components have been clearly observed in the total-ion-yield spectra using time-of-flight mass spectrometry. Relative transition probabilities, excitation energies, and core-hole lifetimes have been measured accurately for the vibronic components of this state. Excited states at higher energies have been also observed. The free radicals have been produced *in situ* by the fast atom-molecule reaction  $H(D) + NO_2 \rightarrow \underline{OH}(\underline{OD}) + NO$  using a microwave technique to generate the H atom. In the case of CS, C 1s and S 2p excited states have been observed. Some of them display a resolved vibrational progression. As for the S 2p excited states, the extent of the vibrational progression, and therefore the change in molecular geometry, varies largely depending on the specific resonant state. Spin-orbit and molecular field splitting effects in S 2p excitation processes are observed for the first time in a diatomic molecule. The CS transient species has been produced *in situ* using the CS<sub>2</sub> precursor and the same microwave technique.

Core-excited states of transient and radical species are often observed as “intermediate fragments” in studies of ultra-fast dissociation processes of core-excited molecules. Our experiments provide, for the first time, a direct information on the inner-shell spectroscopy of those fragments.



**State-to-State Inelastic Collisional Energy Transfer  
in Electronically Excited CH Radicals**

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Electronically excited CH radicals have been prepared in chosen rovibrational levels of the  $A^2\Delta$  and  $B^2\Sigma^-$  states by selective laser excitation. The evolution of the populations in the initial and collisionally populated rovibronic levels has been followed by time and wavelength-resolved fluorescence spectroscopy at rotational resolution.

The collision partners studied include Ar,  $N_2$  and  $CO_2$ . The distinct processes which have been identified and investigated include

- Pure rotational energy transfer (RET) within the  $A^2\Delta$  and  $B^2\Sigma^-$  states.
- Pure vibrational energy transfer (VET) between levels of the  $A^2\Delta$  state.
- Electronic energy transfer (EET) between rovibronic levels of the  $A^2\Delta$  and  $B^2\Sigma^-$  states.

All collision partners induce RET within the  $A^2\Delta$  and  $B^2\Sigma^-$  states. The efficiencies for the molecular colliders are unsurprisingly higher than for Ar. The propensities show a rapid decline in cross-section with increasing  $\Delta N$ . These qualitative results are in line with previous work on these and many other systems. A quantitative analysis of the data is in progress.

CH  $A^2\Delta$ ,  $v=1$  is quite efficiently irreversibly relaxed to  $A^2\Delta$ ,  $v=0$  by  $CO_2$ , at least. Perhaps most interestingly, it is also found to be reversibly transferred to the near-degenerate  $B^2\Sigma^-$ ,  $v=0$  level. Correspondingly,  $B^2\Sigma^-$ ,  $v=0$  is found to be reversibly transferred to  $A^2\Delta$ ,  $v=1$  and irreversibly transferred to the lower-lying  $A^2\Delta$ ,  $v=0$ . The EET processes have comparable cross-sections to pure VET for  $CO_2$  collisions, are also present and currently under quantitative investigation for  $N_2$ , but are much less efficient for Ar.

The rovibrational state-to-state propensities accompanying EET have so far been most fully investigated for  $CO_2$ . The vibrational branching between  $A^2\Delta$ ,  $v=1$  and 0 produced in collisions of  $B^2\Sigma^-$ ,  $v=0$  differs markedly from the predictions of an energy gap scaling law. The rotational distributions in both directions  $B^2\Sigma^-$ ,  $v=0 \rightarrow A^2\Delta$ ,  $v=1$  and 0, and  $A^2\Delta$ ,  $v=1 \rightarrow B^2\Sigma^-$ ,  $v=0$ , appear to be best explained by energetic rather than angular momentum control.

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**Quasiclassical Trajectory Studies of the Dynamics and Stereodynamics of the OH+H<sub>2</sub>  
->H+H<sub>2</sub>O and the Reverse Reaction**

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The simplest elementary reaction involving four atoms is the reaction of H<sub>2</sub> with OH and its reverse process. The dynamics of both have been actively studied, most recently in experiments by Casavecchia et al., Davis et al. and Barnes et al. We performed extensive quasiclassical trajectory calculations to understand the connection between the potential surface and the dynamical features that were observed experimentally.

Our trajectory calculations relied on the WSLFH and OC potential surfaces. The dynamical parameters calculated include the excitation functions, angular distributions, product kinetic and internal energy distributions for both the forward and reverse processes. In addition to reaction from ground state reactants, the dynamics from vibrationally excited reactants were studied. The theoretical data obtained on the new potential surfaces are in much better agreement with the experimental data than the previous surfaces for this reaction.

For the OH + D<sub>2</sub> reaction most recently studied in crossed molecular beams we observed very good agreement between theoretical and experimental final vibrational state distributions, product angular distributions and final translational energy distributions. Remarkable is that the OH stretch mode is very strongly uncoupled from the other modes, and the bend mode is hardly involved in the energy flow during the reaction.

For reaction involving local mode excited states of water with H atoms, we observed that the reaction from OH stretch excited states above the (02)<sup>-</sup> state are characterized by zero activation energy and a capture-type cross section corresponding to attractive interaction between the reactants. In addition, we found that, in agreement with the recent experiments due to Barnes, Sharkey, Sims and Smith, the rate coefficient for reaction from the (04)<sup>-</sup> state is comparable to that of energy transfer.

## Determination of the 0 K enthalpies of formation of radical cations by TPEPICO spectroscopy : application to $\text{CF}_3^+$ , $\text{C}_2\text{F}_5^+$ , $\text{C}_3\text{F}_7^+$ , and $\text{SF}_5^+$

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The determination of the 0 K enthalpy of formation of radical cations, and hence the adiabatic ionisation energy (IE) of some neutral free radicals, is very difficult if ionisation involves a significant change in geometry between neutral and ionised forms. There is then negligible Franck-Condon overlap between  $v=0$  of the neutral and  $v^+=0$  of the cation, making a direct determination of the IE almost impossible. This problem is well known for the  $\text{CF}_3\cdot$  and  $\text{SF}_5\cdot$  free radicals, and recent literature values for the IE of these radicals ('true' values considered to be *ca.* 9.0 and 9.6 eV, respectively) vary by up to 2 eV [1,2].

An alternative approach to measure the enthalpy of formation of the cation is to study the photodissociation dynamics of molecules, where a particular electronic state of the cation is repulsive in the Franck-Condon region. This is true, not only for the *ground* state of  $\text{CF}_4^+$  and  $\text{SF}_6^+$  which dissociate by a direct impulsive mechanism through fluorine-atom loss to  $\text{CF}_3^+$  and  $\text{SF}_5^+$  [3], but also for the *first-excited* state of  $\text{C}_2\text{F}_6^+$  and  $\text{C}_3\text{F}_8^+$  which dissociate impulsively to  $\text{C}_2\text{F}_5^+$  and  $\text{C}_3\text{F}_7^+$  [4,5]. For these four parent neutral molecules, the first ion signal in a threshold photoelectron experiment can only give an *upper limit* to the energy of the first dissociative ionisation pathway, *e.g.*  $\text{SF}_6 \rightarrow \text{SF}_5^+ + \text{F} + \text{e}^-$ . Using tunable vacuum-UV radiation from a synchrotron, however, and TPEPICO time-of-flight spectra to determine the translational kinetic energy (KE) released into the daughter cation and fluorine atom over a range of energies, the KE vs. photon energy data can be extrapolated to zero KE to determine the first dissociative ionisation energy of  $\text{CF}_4$  and  $\text{SF}_6$  [6],  $\text{C}_2\text{F}_6$ , and  $\text{C}_3\text{F}_8$ . We are therefore able to determine the 0 K enthalpies of formation of  $\text{CF}_3^+$ ,  $\text{SF}_5^+$ ,  $\text{C}_2\text{F}_5^+$  and  $\text{C}_3\text{F}_7^+$ , leading to (indirect) values for the IEs of the  $\text{CF}_3\cdot$ ,  $\text{SF}_5\cdot$ ,  $\text{C}_2\text{F}_5\cdot$  and  $\text{C}_3\text{F}_7\cdot$  free radicals. Our results will be compared with values in the literature, and the potential for this technique discussed.

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State-Resolved Electronic Energy Transfer in  
CN( $A^2\Pi$ ) – Ar and He Collisions: High Rotational Levels

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Optical-optical double resonance has been employed to study electronically inelastic transitions from specific, highly rotationally excited  $\Lambda$ -doublet, fine-structure levels of CN( $A^2\Pi$ ), induced by collisions with argon and helium. This study is an extension of our previous work on rotationally inelastic collisions of high CN( $A^2\Pi$ ) rotational levels [1].

High rotational levels of the CN( $X^2\Sigma^+$ ) radical were prepared by 193 nm photolysis of BrCN diluted in slowly flowing Ar at total pressures of 0.5 – 1 Torr. After a suitable delay, specific fine-structure  $\Lambda$ -doublet levels of CN( $A^2\Pi$ ,  $v = 3$ ,  $N = 60$ -63) were prepared by excitation with a pulsed dye laser on various rotational lines in the  $A^2\Pi - X^2\Sigma^+$  (3,0) band. Collisionally populated levels were probed after a short delay by laser fluorescence excitation in the  $B^2\Sigma^+ - A^2\Pi$  (3,3) and  $B^2\Sigma^+ - X^2\Sigma^+$  (3,7) bands. State-to-state rate constants were determined for transitions between specific levels in the  $A^2\Pi$   $v=3$  initial and nearly isoenergetic  $X^2\Sigma^+$   $v=7$  final vibronic manifolds.

A crossing of the  $A^2\Pi$   $v = 3$   $F_1f$  rotational/fine-structure manifold with the  $X^2\Sigma^+$   $v = 7$   $f$  manifold occurs at  $N = 62$ . We have investigated the importance of this "gateway" in facilitating collision-induced electronic transitions between these manifolds. The total removal rate constant for the perturbed  $N = 62$  level in collisions with argon is substantially larger than for those of neighboring unperturbed levels, indicative of the magnitude of the perturbation-assisted  $A \rightarrow X$  rate constants. Moreover, the final-state distribution is strongly dependent on the identity of the initial state. Collisional propensities, similar to those observed in rotationally inelastic collisions [1], were found for unperturbed initial levels. The  $A \rightarrow X$  rate constants for CN–He collisions were found to be much smaller than for CN–Ar collisions, indicative of the weaker coupling between the electronic states induced by the approach of He vs. Ar [2].

The experimental state-to-state  $A \rightarrow X$  rate constants will be compared with theoretical rate constants computed on the basis of *ab initio* potential energy surfaces [2].

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### Photodissociation of the OH radical using velocity map imaging

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Velocity Map Imaging is used to study the photodissociation of OH radicals produced in a pulsed molecular beam with an electric discharge. H atoms and O atoms are detected using (2+1) REMPI (resonance enhanced multiphoton ionization) following photoexcitation of OH via the lower vibrational levels of the  $A^2\Sigma^+$  state. Information on the rapid predissociation of this important electronic state, used for laser induced fluorescence diagnostics, is obtained from the angular and speed distributions provided by the velocity map images. Preliminary data on reactive scattering of OH with hydrogen halides using imaging detection will be mentioned.

## High-Resolution ZEKE-Photoelectron Spectroscopy of Hydrocarbon Radicals

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The ionisation energy (IE) is one of the most important thermochemical properties of molecules, because it permits to deduce molecular binding energies through thermochemical cycles. In the past, IE's of reactive intermediates, like hydrocarbon radicals, have been determined mostly by conventional photoelectron spectroscopy or photoionisation efficiency measurements. However, the accuracy is often insufficient, given the importance of radicals in many high-energy environments, like combustion engines, crackers or interstellar space.

We recently investigated the hydrocarbon radicals allyl ( $\text{C}_3\text{H}_5$ ), propargyl ( $\text{C}_3\text{H}_3$ ) and t-butyl ( $\text{C}_4\text{H}_9$ ) by high resolution ZEKE photoelectron spectroscopy. The spectra yielded very accurate IE's, as well as cationic vibrational frequencies.

Due to the absence of any long-lived intermediate state, the ZEKE spectra of propargyl (IE=  $69953\text{ cm}^{-1}$ ) and t-butyl were obtained by nonresonant two-photon excitation.

In the case of allyl (IE=  $65762\text{ cm}^{-1}$ ), on the other hand, spectra were recorded through the intermediate UV states,  $\text{B } ^2\text{A}_1$  and  $\text{C } ^2\text{B}_1$ , at around 5 eV. The states decay within 20 ps or less by internal conversion, as shown by picosecond time-resolved photoelectron spectroscopy. The ZEKE spectra provide additional evidence for a pseudo Jahn-Teller interaction between the B- and the C-state, leading to a geometrical distortion of the B-state. The results demonstrate (a) that radicals are ideally suited to study non-adiabatic interactions, and (b) that ZEKE spectroscopy permits to elucidate intermediate state structure and couplings.

## An injection seeded, single frequency Optical Parametric Oscillator for high resolution molecular spectroscopy.

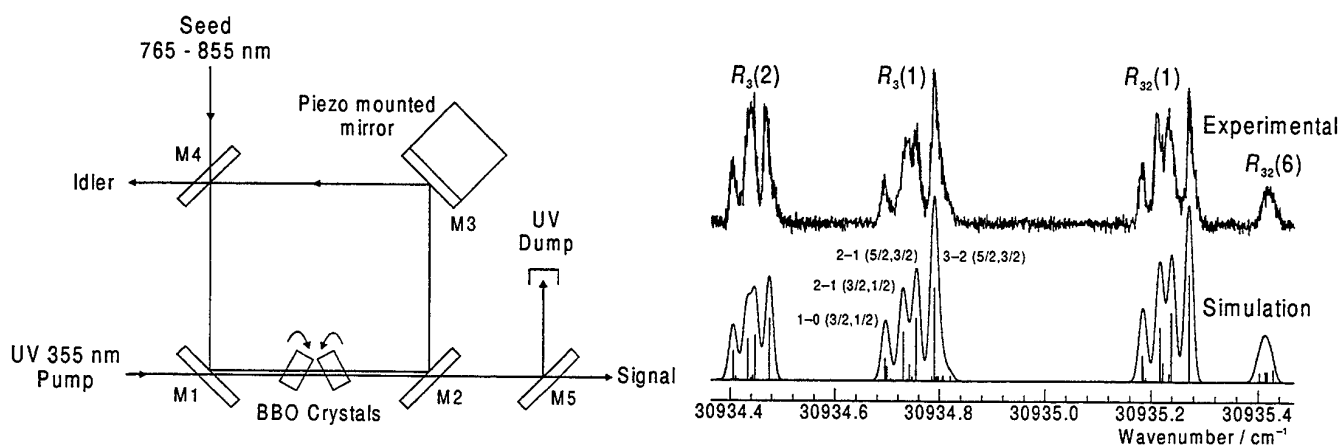
James A.J. Fitzpatrick, Robert Burrows, Oleg V. Chekhlov, John M.F. Elks and  
Colin M. Western

*School of Chemistry, Cantock's Close, Bristol, BS8 1TS, UK*

Stephen H. Ashworth

*School of Chemical Sciences, University of East Anglia, Norwich, NR4 7TJ, UK*

We describe the construction of an all solid-state, single frequency, pulsed optical parametric oscillator and its application to high resolution molecular spectroscopy. The OPO system is based on two BBO crystals enclosed in a ring cavity, which is injection seeded by a commercial external cavity diode laser in the near infrared. The OPO is capable of generating narrow bandwidth ( $\sim 130$  MHz) tuneable light at the seed frequency and simultaneously at the visible signal frequency. By frequency doubling either the signal or the idler outputs, or sum frequency mixing either of these with 355 or 532 nm a wide range of UV wavelengths are available. Details of construction are presented along with measurements of linewidths, pulse lengths, and pump power dependence. A schematic of the OPO resonator is shown below. An application of this system to the investigation of hyperfine structure in the PF radical [1] is also presented here. A spectrum showing clear hyperfine splittings is shown below, and these are interpreted in terms of the bonding in PF. Spectra of other species are also presented, including a preliminary high resolution study of the BBr radical.



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**ABSTRACTS  
OF  
CONTRIBUTED PAPERS**

*Posters*



## Laser induced fluorescence study of the $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$ vibronic bands of $C_3$

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The laser induced fluorescence (LIF) spectra for the  $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$  band of the  $C_3$  radical have been observed in the range 25500-30000  $\text{cm}^{-1}$  under supersonic jet-cooled conditions.  $C_3$  was generated with an electric discharge in a 0.9% mixture of  $C_2H_2$  in Ar with a backing pressure typically between 1-2 atm giving a rotational temperature around 5-10K. More than one hundred vibronic bands were recorded, many of them new, including some very weak transitions. Several of the bands have been recorded with a new narrow bandwidth injection seeded OPO described in another poster. Careful analysis of rotational structure has produced more precise data for many of the previously reported bands. We are currently developing a model to assist in assigning these transitions by calculating both the band origins and rotational constants and to determine the potential energy surface for this system from the complex vibronic structure. Preliminary results from this will be presented in the poster.

## Nanosecond and Femtosecond Probing of the Dynamics of the UV-Photodissociation of Perfluoroethyl iodide $C_2F_5I$ .

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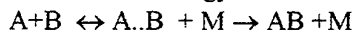
The ns photodissociation of perfluoroethyl iodide  $C_2F_5I$  at 266 nm has been studied by using the R2PI technique. Recoil anisotropy parameters as well as average translational energy of the I atoms in the fine structure states  $^2P_{1/2}$  and  $^2P_{3/2}$  have been determined. The ground state atoms  $I(^2P_{3/2})$  were found to appear mainly due to the adiabatic transition from the primarily excited  $^3Q_0$  state. The fs pump-dump technique in combination with ns R2PI probing of the fragments  $I(^2P_{1/2})$  and  $I(^2P_{3/2})$  and time-of-flight mass spectrometry have been applied to probe the early stage dynamics of the  $C_2F_5I$  molecule on the excited state  $^3Q_0$  potential energy surface (PES). The evolution-time of the excited molecule to the point where the energy gap between the excited state  $^3Q_0$  and the ground state potential energy surfaces drops to a value of about  $12440\text{ cm}^{-1}$  was found to be  $52 \pm 13\text{ fs}$ . This time corresponds to about  $0.8\text{ \AA}$  extension of the C-I bond distance. The molecular dynamics simulation with DFT calculated ground state PES and  $^3Q_0$  PES with the shape calculated for methyl iodide found in literature gives reasonable agreement with the experimental result for the evolution-time.

# Rare gas halides as a prototypical system for studies of the role of intersystem crossings and vibrational excitation of reagents in recombination mechanism

Vadim A. Alekseev

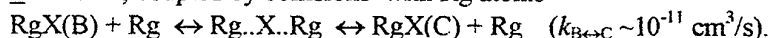
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Internal energy of A..B complex formed in the first stage of radical recombination

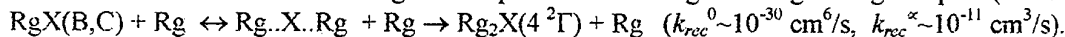


is  $\sim kT$  above the ground state dissociation asymptote. Complexity of A..B electronic structure in this energy range is a major obstacle for theoretical investigation of recombination dynamics. For instance,  $\text{NO}_2$ , a model system for recombination and dissociation studies,<sup>1</sup> has 12 electronic states correlating with six  $\text{NO } ^2\Pi_{1/2, 3/2} + \text{O } ^3\text{P}_{0,1,2}$  asymptotes lying within  $\sim 250 \text{ cm}^{-1}$ . In the present work we show that excimer molecules formed from a halogen atom and rare gas atoms owing to captivating simplicity of their electronic structure and kinetic could be a source of valuable information for further elucidation of the recombination mechanism.

The family of rare gas halides includes  $\sim 10$   $\text{RgX}$  dimers and  $\sim 20$   $\text{Rg}_2\text{X}$  and  $\text{Rg}'\text{RgX}$  trimers. Dimers have two close lying excited electronic states,  $B \ ^2\Sigma_{1/2}$  ( $\tau_{\text{rad}} \sim 10 \text{ ns}$ ) and  $C \ ^2\Pi_{3/2}$  ( $\tau_{\text{rad}} \sim 100 \text{ ns}$ ),  $T_e(B) - T_e(C) = \pm 200 \text{ cm}^{-1}$ , coupled by collisions with Rg atoms



Recombination of dimer with rare gas atom proceed via a long-lived  $\text{Rg}..X.. \text{Rg}$  complex ( $\tau \sim 100 \text{ ps}$ )<sup>2</sup>



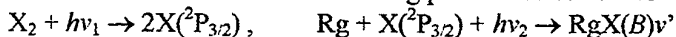
Kinetic of  $\text{Rg}_2\text{X}(4 \ ^2\Gamma)$  formation and loss in a binary  $\text{X}_2/\text{Rg}$  mixture is remarkably simple:  $k_{\text{rec}}^0$  and  $k_{\text{rec}}^\infty$  can be easily deduced from the emission intensities ratio

$$I_{\text{Rg}_2\text{X}}/I_{\text{RgX}} = \tau_{\text{rad RgX}} k_{\text{rec}}[\text{Rg}]^2 / (1 + \tau_{\text{rad Rg}_2\text{X}} k_Q[\text{X}_2]),$$

where  $k_{\text{rec}}$  is pressure-dependent recombination rate coefficient,  $k_Q$  is rate constant of  $\text{Rg}_2\text{X}(4 \ ^2\Gamma)$  quenching by  $\text{X}_2$ . The  $4 \ ^2\Gamma$  state ( $\tau_{\text{rad}} \sim 200 \text{ ns}$ ) is most stable in the  $\text{C}_{2v}$  geometry ( $D_e \sim 0.6 \text{ eV}$ ) and is a lower in energy component of two mixed electronic states, correlating with the C and B states of dimer. The upper component is repulsive in the  $\text{C}_{2v}$  geometry and weakly bound in the linear geometry. The second state of trimer correlating with  $\text{RgX}(C)$  is purely repulsive.<sup>3</sup>  $\text{Rg}'\text{RgX}$  trimers have weaker binding energy in the  $4 \ ^2\Gamma$  state ( $\sim 0.25 \text{ eV}$ ); other properties and kinetic are similar to  $\text{Rg}_2\text{X}$ .

The degree of A..B electronic states mixing (ergodicity) and concomitant nonadiabatic effects in recombination dynamics are of principal interest. Using rare gas halides as a model, the limiting cases of weak and strong mixing will be discussed with an emphasis on the following questions: (i) relation between  $k_{B \leftrightarrow C}$  and  $k_{\text{rec}}^\infty$  for the case of strong mixing as an extension of the relation between  $k_{\text{rec}}^0$  and vibrational relaxation rate constant<sup>4</sup> for the case when recombination proceed on a single potential energy surface. (ii) collision-induced transitions between strongly bound (long-lived) and dissociative electronic states of  $\text{Rg}..X.. \text{Rg}$  for the case of weak mixing and their influence on  $k_{\text{rec}}^0$  and  $k_{\text{rec}}^\infty$ . Some aspects of rare gas halides kinetics in ternary  $\text{X}_2/\text{Rg}/\text{Rg}'$  mixtures ( $P_{\text{Rg}} \ll P_{\text{Rg}'}$ ), including competition between the energy-transfer and "chaperone" recombination mechanisms, will be discussed too.

State-selective excitation using photodissociation followed by laser-assisted recombination (LAR)<sup>5</sup>



at low and high Rg pressures opens a promising opportunity to study the scaling of  $k_{\text{rec}}^0$  and  $k_{\text{rec}}^\infty$  with the initial vibrational excitation. Similar experiment can not be easily performed for the radical recombination in bath gases, because numerous A+M and B+M state changing collisions thermalize distribution prior A+B complex forming collision. Use of some other laser-assisted methods in combination with LAR may lead to development of techniques for studies of recombination dynamic on the state-to-state level.

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## Sub-millimeter spectra of HCS and DCS

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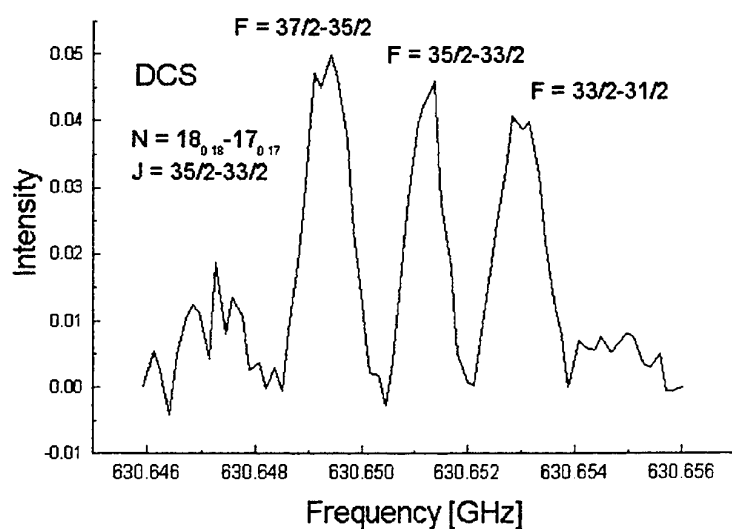
And

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The HCS radical is one of the potential candidates of inter-stellar molecules. Its rotational spectrum was first observed using the Fourier transform millimeter spectrometer in the frequency region of 40 GHz (JCP **108**, 8859 (1998)). The millimeter and sub-millimeter rest frequencies of HCS are useful in searching for this radical with radio-telescopes. The measurements have been extended to 240 – 645 GHz range for both HCS and DCS.

The HCS radical is produced in a free-space cell discharging a gaseous mixture of H<sub>2</sub>S and CO. Only the *a*-type  $K=0$  transitions have been observed so far. However, through an analysis of a perturbation caused by a spin-rotation interaction,  $\varepsilon_{ab} (N_a S_b + N_b S_a)$ , that connects the  $K=0$  and  $K=1$  levels, the *A* rotational constant has been determined with reasonable accuracy for DCS. We will report obtained molecular constants and discussion about the molecular structure of HCS.



<sup>1</sup> National Space Development Agency of Japan (NASDA), Postdoctoral fellow

## The dynamics of the $O(^1D)+H_2$ reaction: Theoretical studies and comparison with experimental results

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The newest experiments on the title reaction and its isotopic variants obtained with an unprecedented level of detail [1,2] constitute a challenge for theoretical calculations. In this communication we report adiabatic quasi-classical trajectory (QCT) and quantum mechanical (QM) calculations on the most recent  $1A'$  and  $1A''$  potential energy surfaces (PES) for this system by Dobbyn and Knowles [2,3]. Non-adiabatic trajectory surface hopping (TSH) calculations on the  $1A'$  and  $2A'$  PESs [3] are also presented. The present study focuses on the calculation of state-resolved integral and differential cross sections and product rotational angular momentum polarization, which are compared with the experimental data by the groups of Yang and Brouard. The collision energy distribution in the crossed beam experiments of Yang and co-workers is very narrow and centered around 0.056 eV, distinctly below the lowest energy classical barrier ( $\approx 0.10$  eV) for reaction on the  $1A''$  and  $2A'$  excited PESs. The measurements lead to differential cross sections (DCS) with nearly backward-forward symmetry and to approximately statistical distributions of the internal states of the products. The extensive set of experimental products' state distributions as a function of laboratory scattering angle can be simulated very well with the results of both the QCT and QM calculations. As expected, only the  $1A'$  PES is found to be relevant under the conditions of this experiment. In contrast, the collision energy distribution of the experiments of Brouard and co-workers is broad, centered at 0.12 eV and with a FWHM of 0.16 eV, and thus a significant number of collisions will take place at energies higher than the barrier for reaction on the excited surfaces. In order to simulate the measured OH rotational distributions, the theoretical cross sections for reaction on the  $1A''$  must be considered. The dynamics on this repulsive PES is governed by a direct mechanism and leads to a much lower OH rotational excitation than that on the attractive  $1A'$  PES. More importantly, the product vibrational distribution resulting from the reaction on the excited  $1A''$  PES is strongly inverted in contrast with that occurring on the  $1A'$  PES. The qualitative shape of the rotational QM and QCT distributions is similar, but in this case the best agreement with experiment is obtained with the QM results. Results for the isotopic variants  $O(^1D)+D_2$  and  $O(^1D)+HD$  will be also presented.

## References

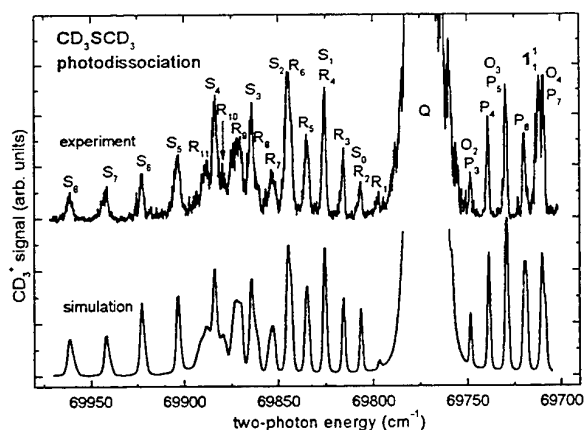
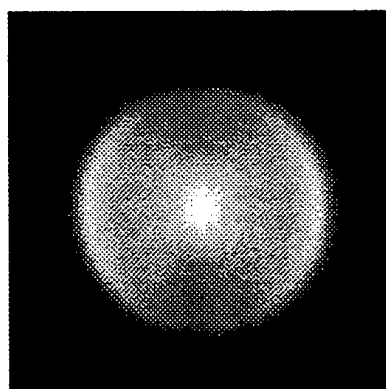
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## THE PHOTODISSOCIATION OF DIMETHYL SULFIDE FROM THE FIRST ABSORPTION BAND

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The photodissociation of dimethyl sulfide ( $\text{CH}_3\text{SCH}_3$  and  $\text{CD}_3\text{SCD}_3$ ) from the first absorption band at wavelengths 220-232 nm has been investigated in pump-probe experiments. The resonance enhanced multiphoton ionization (REMPI) technique with time-of-flight mass spectrometry (TOFMS) of the  $\text{CH}_3/\text{CD}_3$  radicals has been employed to determine recoil energy distributions and the anisotropy parameter  $\beta$ , and to study the rovibrational state population of the nascent  $\text{CH}_3/\text{CD}_3$ . In addition, translational energy and recoil angle distributions have been determined by velocity map ion imaging of  $\text{CH}_3/\text{CD}_3$ . The measurements indicate that the S-C bond photolysis yields strongly anisotropic product scattering distributions characterized by  $\beta$  parameters close to the limiting value for



*Velocity map ion image (left) and REMPI spectrum (right) of the methyl fragment*

perpendicular transition (-1.0). The product recoil energy distributions and REMPI spectra indicate that methyl and methylthio fragments are born internally cold but with substantial translational excitation. A full account of the most relevant results will be presented at the conference.

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## UV Photo-induced Decarboxylation of Organic Peroxides: Picosecond IR and Femtosecond UV-NIR Studies

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Due to their widespread use as initiators in free radical polymerizations, fundamental interest centers on the photo-induced decomposition of organic peroxides. A detailed study on the mechanisms and the rate constants of the ultrafast decarboxylation process of various areneperoxides is presented. After UV-photodissociation of the molecules the formation and the decay of product aryl as well as intermediate aryloxy radicals could be observed in real-time using a femtosecond (fs) Titan-Sapphire laser system with probe wavelengths tunable from 300-900 nm. Broad absorption bands of decarboxylating aryloxy radicals were detected ranging from the UV to the nearIR. Product radicals (e.g. benzyl or phenoxy radicals) exhibit spectrally narrow absorption features ( $\pm 5$  nm) in the UV range. The impressive correlation of decaying and rising transients clearly indicates that educt and product molecules of the same chemical process (i.e. the decarboxylation of aryloxy radicals) were observed. Further, the results are fully consistent with picosecond (ps) UV-pump-midIR-probe experiments which were carried out in our work-group using a ps-DFDL laser system. Transient spectra of the asymmetric stretching mode ( $\nu_3$ ) of  $\text{CO}_2$  allowed us to observe the ps formation and to estimate the vibrational excitation in the  $\text{CO}_2$  fragment after decomposition.

Ab-initio calculations on the structure and energetics of educt and product radicals as well as for the transition state for the decarboxylation processes are presented. RRKM calculations on the basis of these values give additional information, whether the observed dynamics could be described by barrier-dependent decarboxylation from the ground state of the intermediate radicals or may include direct decarboxylation from an excited state of the peroxide.

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## Cavity Enhanced Diode Laser Absorption Spectroscopy for Highly Sensitive Detection

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Absorption techniques using high finesse optical cavities have recently become popular for detection as they benefit from the enhanced effective pathlength available to the light when it is trapped inside an optical cavity and retraces the same path through the sample many times. The cavity enhanced technique that we employ is very simple and avoids the use of any equipment other than the most basic devices used in a laboratory and as such it requires a lot less technical expertise to carry out, uses a relatively cheap setup and has potential for application to compact laser based detection systems. The technique may be viewed as a type of multipass absorption spectroscopy that has the advantage of continuous data acquisition over other cavity based methods such as CRDS.

In a recent Letter we demonstrated the application of the technique of diode laser spectroscopy by cavity enhanced absorption to the detection of methane. Here we will show its application to the detection of formaldehyde on its  $2\nu_3$  overtone centred on  $5650\text{cm}^{-1}$  along with a further enhancement of the detectivity of this technique by the use of phase sensitive detection. However, the available literature on formaldehyde in this spectral region is sparse and, to our knowledge, there has been no detailed study of the rotational structure of this transition. Thus we also demonstrate the application of this technique to the determination of absolute absorption cross sections for some of the rotationally resolved peaks of formaldehyde in this band by calibration with another species.

Furthermore, we shall demonstrate the use of this technique in the detection of the methyl radical *via* its  $2\nu_3$  overtone at approximately  $1.6\text{ }\mu\text{m}$ . surprisingly, this transition has not been studied before and this cavity enhanced technique will be used to measure absorption cross sections for this transition, calibrated by the kinetics of a well studied reaction:  $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ . Methyl plays an important rôle in diamond formation in  $\text{CH}_4/\text{H}_2$  plasmas and CEAS will be used to investigate methyl concentrations in a modified rf plasma reactor.

We shall also report on the use of diode lasers to detect the OH radical, by using an enhancement cavity to frequency double the output of a cooled diode laser at 620 nm.



## Crossed beam studies of the prototype *insertion* reactions $\text{N}(^2\text{D})+\text{H}_2$ and $\text{C}(^1\text{D})+\text{H}_2$ : Dynamics of formation of $\text{NH}(\text{X}^3\Sigma^-)$ and $\text{CH}(\text{X}^2\Pi)$ radicals

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Great strides have been made over the last 10 years on the understanding, both experimental and theoretical, of simple abstraction reactions, such as  $\text{H}+\text{H}_2$ ,  $\text{F}+\text{H}_2$ , and  $\text{Cl}+\text{H}_2$ .<sup>1</sup> Recently, a significant effort has been devoted to reaching a similar understanding of the more complex *insertion* reactions, the common characteristic of which is that they occur on a PES with a deep well associated with a strongly bound species.<sup>1,2</sup> The most popular, prototype insertion reaction is  $\text{O}(^1\text{D})+\text{H}_2$ , which proceeds over the potential energy surface(s) (PES) of  $\text{H}_2\text{O}$ .<sup>1,2</sup>

In order to deepen our understanding of *insertion* dynamics, we have recently extended our crossed beam investigations to other two prototypical insertion reactions, namely,  $\text{N}(^2\text{D})+\text{H}_2$  and  $\text{C}(^1\text{D})+\text{H}_2$ , which occur on the PES of the  $\text{NH}_2$  and  $\text{CH}_2$  radicals, respectively. We exploit the novel capability of generating continuous supersonic beams of  $\text{N}(^2\text{D})$  and  $\text{C}(^1\text{D})$  atoms.<sup>3,4</sup>

In previous work from our laboratory on the isotopic variant  $\text{N}(^2\text{D})+\text{D}_2$ , the differential cross section was measured at  $E_c=3.8$  and  $5.1$  kcal/mol.<sup>5</sup> The scattering results were presented together with QCT calculations on an accurate *ab initio* ground state PES. In spite of a general good agreement, some discrepancies between experimental results and QCT calculations were visible and pointed to the inaccuracy of the PES and/or of the QCT treatment; we recall that the reaction has an entrance barrier and that tunneling is possible. Exact QM scattering calculations on the same PES have been recently performed.<sup>6</sup> In order to directly compare our experimental results with these state-of-the-art QM calculations, the first for an insertion reaction, we have performed new experiments on the isotopic variant  $\text{N}(^2\text{D})+\text{H}_2$  at one  $E_c$  investigated by Honvault and Launay. The excellent agreement between experimental results and QM calculations points to a substantial accuracy of the *ab initio* PES.

The reaction  $\text{C}(^1\text{D})+\text{H}_2$  was investigated at two different collision energies,  $E_c=1.86$  and  $3.8$  kcal/mol, and is found to proceed by *insertion* forming an excited  $\text{CH}_2$  (methylene) radical which decomposes into  $\text{H}+\text{CH}$  (methylidene). The  $\text{CH}(\text{X}^2\Pi)$  product is formed predominantly in  $v'=0$  at the lowest  $E_c$ , while also some  $\text{CH}(v'=1)$  is observed at the higher  $E_c$ . The micromechanism and the product energy partitioning into translation, vibration and rotation are characterized. The results at  $E_c=1.86$  kcal/mol were compared with Phase-Space-Theory predictions, which pointed to a not fully statistical behavior. The results for this prototype *insertion* reaction are being compared with exact, quantum scattering calculations on a new *ab initio* potential energy surface.<sup>7</sup>

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## Crossed beam and quantum dynamical studies of prototype *abstraction* reactions: $\text{Cl}(^2\text{P}_{3/2,1/2}) + \text{H}_2$

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In our laboratory, the crossed molecular beam technique with mass spectrometric detection has been successfully applied over a number of years to the study of simple prototypical reactions.<sup>1</sup> The aim has been to reach for other systems the level of detailed comparison between state-of-the-art experiment and state-of-the-art theory as done for the well-known three-atom reactions  $\text{H}+\text{H}_2$  and  $\text{F}+\text{H}_2$ .

The reaction  $\text{Cl}(^2\text{P})+\text{H}_2$  belongs to the same family of *direct abstraction* reactions as  $\text{H}+\text{H}_2$  and  $\text{F}+\text{H}_2$ . We performed a first series of scattering experiments on the two variants  $\text{Cl}(^2\text{P})+\text{H}_2$  and  $\text{Cl}(^2\text{P})+\text{D}_2$ ; the experimental results were compared with quantum (QM) scattering and quasiclassical trajectory (QCT) calculations on the most accurate potential energy surface (PES) available at that time, the G3 PES.<sup>2</sup> More recent experimental results by Liu<sup>3</sup> pointed to some inaccuracy of the G3 PES and a new surface was developed by Bian and Werner (BW2).<sup>3</sup> The new surface has overcome some of the G3 shortcomings and well predicts *i*) the effect of initial rotational excitation of  $\text{H}_2$  and *ii*) the  $\text{HCl}/\text{DCl}$  branching ratio for the  $\text{Cl}+\text{HD}$  reaction.<sup>3</sup> QM scattering calculations on the BW2 PES have also well reproduced our experimental data and the effect of the initial rotational excitation of  $\text{H}_2/\text{D}_2$  was especially confirmed in the case of the low collision energy ( $E_c$ ) experiments.<sup>4</sup> Quasiclassical trajectory calculations were performed as well.<sup>4</sup>

With the aim of better elucidating the effect of the initial rotational excitation and tackling the possible reactivity of the spin-orbit excited state,  $\text{Cl}(^2\text{P}_{1/2})$ , we have performed a new series of experiments on  $\text{Cl}(^2\text{P})+\text{H}_2$  at  $E_c$  close to the threshold ( $E_c=3.75$  and  $4.25$  kcal/mol) and with a more favorable kinematics. The experimental results will be discussed in the light of scattering calculations on new multiple PESs by Capecchi and Werner, where the spin-orbit coupling is explicitly taken into account.

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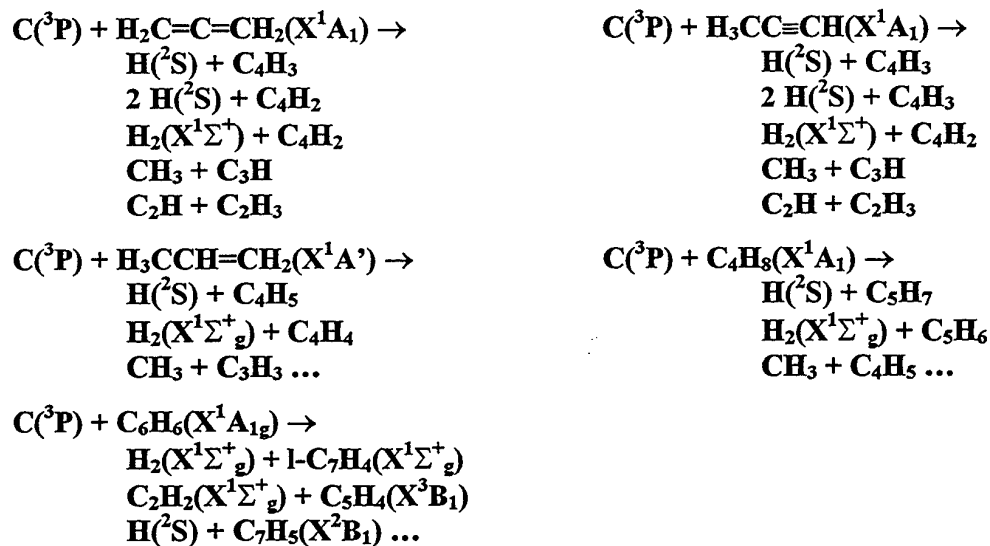
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**Reaction of carbon atoms,  $C(2p^2, ^3P)$  with  
 $C_3H_4$  (allene and methylacetylene),  $C_3H_6$  (propylene),  
 $C_4H_8$  (trans-butene) and  $C_6H_6$  (benzene):  
Overall rate constant and relative atomic hydrogen production.**

**Astrid Bergeat and Jean-Christophe Loison**

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These reactions are believed to play a key role in combustion and interstellar chemistry. Their overall rate constants have been determined by I. R. Sims and I. W. Smith down to 15 K and by D. Husain and co-workers at room temperature. However, the main problem is that these reactions have several exoergic product channels which could not be clearly identified in the absence of a clean source of atoms.



Our studies of the kinetics and branching ratio determinations are conducted in a low-pressure fast-flow reactor at 300 K. The C atoms were produced by the reactions of  $CBr_4$  with potassium atoms. The overall rate constants have been determined following the decay of the  $C(^3P)$  atoms by resonance fluorescence in the vacuum ultraviolet, the hydrocarbons being introduced in excess. The results are given after corrections due to the axial and radial diffusions. The product branching ratios have been determined over the pathways yielding H atoms, by resonance fluorescence in the vacuum ultraviolet. The resonance lamp was carefully characterised and the observations have been supplemented with chemiluminescence detection.

FOURIER TRANSFORM EMISSION SPECTROSCOPY OF NEW ELECTRONIC  
TRANSITIONS OF VN AND VOR. S. RAM<sup>a</sup>, P. F. BERNATH<sup>b</sup> and S. P. DAVIS<sup>c</sup><sup>a</sup>*Department of Chemistry, University of Arizona, Tucson, AZ 85721*<sup>b</sup>*Department of Chemistry, University of Waterloo, Waterloo, ON, Canada N2L 3G1*<sup>c</sup>*Department of Physics, University of California, Berkeley, CA 94720*

The emission spectra of VN and VO have been investigated in the 3700-18300 cm<sup>-1</sup> region using a Fourier transform spectrometer. The spectra of both these species were observed in the same experiment from the microwave excitation of VOCl<sub>3</sub> vapor in active nitrogen. Several new bands were observed and assigned to new electronic transitions of VN and VO. For VN, two new electronic transitions were observed with their 0-0 bands near 14293 cm<sup>-1</sup> and 5267 cm<sup>-1</sup>. These transitions have been assigned as the c<sup>1</sup>Π - a<sup>1</sup>Δ and d<sup>1</sup>Σ<sup>+</sup> - b<sup>1</sup>Σ<sup>+</sup> transitions, respectively. The d<sup>1</sup>Σ<sup>+</sup> state of VN is the only known singlet state to date which was seen previously from the d<sup>1</sup>Σ<sup>+</sup> - X<sup>3</sup>Δ<sub>1</sub> transition near 16220 cm<sup>-1</sup> by Simard et al. [J. Mol. Spectrosc. **136**, 44 (1989)]. For VO, the 1<sup>2</sup>Φ - 1<sup>2</sup>Δ transition near 5545 cm<sup>-1</sup> has been observed for the first time, although the 1<sup>2</sup>Φ and 1<sup>2</sup>Δ states have previously been seen by Merer et al. [J. Mol. Spectrosc. **125**, 465, (1987)] from other transitions. A rotational analysis of the new bands provides valuable information on the low-lying electronic states of VN and VO.

DiRef, A DATABASE OF REFERENCES ASSOCIATED WITH THE SPECTRA OF  
DIATOMIC MOLECULES

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For some years now we have been compiling references of diatomic molecules with the ultimate (but still distant) goal of a revision of Huber and Herzberg's classic book "Constants of Diatomic Molecules." Our work is based largely on the Berkeley Newsletters, but with additions and corrections. DiRef (Diatomic Reference Database) currently consists of about 30,000 references including titles covering the period of 1974 - 2000. The starting year was chosen to ensure adequate overlap with the references found in Huber and Herzberg. An on-going project (about half-completed) is the addition of all references in Huber and Herzberg to DiRef. We endeavor to keep DiRef current through regular up-dates several times per year. DiRef is available on the Web at <http://diref.uwaterloo.ca/>.

**On product state distributions in elementary unimolecular reactions:  
Beyond phase space theory and the adiabatic assumption**

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**Abstract** — We propose a simple dynamically corrected statistical treatment of state distributions in the products of elementary unimolecular reactions involving efficient energy transfers between rotation and translation motions on the way from the transition state (TS) to the products. For, phase space theory (PST) or the adiabatic channel model (ACM) — the only statistical approaches of final state distributions — may not be applicable to such processes. We thus analyse and model how one given nascent fragment perturbs the rotation of the other one. A remarkable fact is the one-to-one relation between the perturbation and a coefficient  $z_0$ , related in a simple way to the mechanical parameters of the system. Transition state theory (TST) combined with our model — the linear transformation model (LTM) — leads to the desired treatment of product state distributions. Its predictions are in good agreement with dynamical calculations. We also show that there is a close relation between the final shape of state distributions and the angular dependence of the potential energy at the TS.

P. Larregaray, L. Bonnet and J. C. Rayez, J. Chem. Phys. 114 (2001) 3349

## VISIBLE SPECTROSCOPY OF POLYCYCLIC AROMATIC HYDROCARBONS IONIC DERIVATIVES : APPLICATION TO ASTROPHYSICS

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The understanding of physical and chemical processes in the interstellar medium is currently an important challenge for our Universe knowledge since these processes are involved in the control of stars and planets formation.

Polycyclic Aromatic Hydrocarbons (PAHs) are now recognized as an important constituent of the interstellar medium gaseous phase, mainly through observations of their IR emission bands. This family of molecules and in particular their ionic and radical derivatives seems to be one of the most promising candidates for identification of Diffuse Interstellar Bands (DIBs). These absorption bands, observed - throughout the visible and near infrared spectral range - over spectra of stars masked by gas cloud, were first discovered in 1922. Their properties indicate that DIBs could originate from gaseous phase carbonaceous molecules. The possible identification of PAHs as molecules responsible for these bands must be done through direct comparison with PAHs spectra recorded in conditions as close as possible to those of the interstellar medium.

These low temperature and collision-free conditions can be recreated in the laboratory with supersonic beams. The spectroscopic methods used to probe the beam must be very sensitive since ions cannot be produced in large quantities. In our laboratory, PAH ions are formed by resonant two-photon ionization with two tunable lasers, and the absorption of a third laser beam is detected by a time-of-flight mass spectrometer. This mass spectroscopic detection supposes that the photon absorption induces a change in the molecule charge or mass, which cannot be produced by a visible photon. This problem was solved by ionizing a van der Waals complex formed by the association of the molecule under study and an argon atom, the third photon absorption causing argon departure. The PAH cation visible spectrum is recorded while monitoring the fragmentation ratio as a function of the energy of this photon. These absorption signatures give acces to the searched spectrum, since rare gas atom adsorption is a very small perturbation for the electronic transitions. With this technique, several spectra of PAH cations could be obtained, spectra which were compared with DIBs spectra seen in the litterature. At the Laboratoire de Photophysique Moléculaire, spectra of six different PAH cations have been obtained up to now, with PAH cations cold, isolated and in the gas phase. The newest results will be presented.

Moreover, two observation campaigns with the Télescope Bernard Lyot at the Pic du Midi were carried out and should allow us to perform a systematic search for correspondence between the bands observed in experimental spectra and in astronomical spectra. The data processing is currently in progress. But some improvements in the observational protocole have already shown their efficiency : a very good correction of the atmospheric absorption lines has been obtained, and a high signal-to-noise ratio - so useful for our purpose - emerges as a result of averaging multiple spectra acquired in successive optimal exposures.

A CHEMOMETRIC ANALYSIS OF THE MOLECULAR BROMINE  
PHOTODISSOCIATION

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Photodissociation dynamics of diatomic molecules still present some unexplored aspects which continue intriguing research groups. In spite of many experimental and theoretical investigations concerning the description of this kind of process with dihalogens molecules, their dissociation is often related to interacting crossing states. This fact results in interchange of population in the states involved, leading to a increasing level of difficulty in obtaining some selectivity in the products formation. In this work we employed chemometric analysis techniques to predict the effects of the simultaneous variation of parameters related to molecular bromine photodissociation in a time-dependent quantum picture. The investigated photodissociation processes are induced by ultra-short monochromatic laser pulses, which produce excitations from the  $X(^1\Sigma_g)$  ground state to the excited  $B(^3\Pi_{o^+})$  (bound) and  $\Pi(^1\Pi_{1u})$  (repulsive) crossing states. The parameters taken into account are: pulse width, isotopic combination, and kinetic coupling width. Pulses widths of 24, 48 and 96 femtoseconds were employed to the isotopic combinations Br(79)-Br(79), Br(79)-Br(81) and Br(81)-Br(81) with kinetic coupling width values  $\Delta r=0.020$ , 0,058 and 0,116 (in atomic units). The best combination of the above mentioned parameters lead to a configuration which corresponds to a significant selectivity ( $\approx 4$ ) in the Br/Br\*+Br products branching ratio.



## Far-Infrared Laser Magnetic Resonance Spectroscopy : Further Progress

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and .

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Recent work in the field of far-infrared Laser Magnetic Resonance (LMR) has focussed on experiments at shorter wavelengths between 100 and 40  $\mu\text{m}$  (100 to 250  $\text{cm}^{-1}$ ). Many new laser lines have been discovered in this range and some of them have been used to record spectra of free radicals. Fine-structure transitions in molecules with larger spin-orbit splittings are now accessible. Some recent observations of this type on the FeH radical in its  $X^4\Delta$  state and of  $\text{HF}^+$  in its  $X^2\Pi$  state will be presented. The lowest two fine-structure splittings for FeH are 190.8 and 234.9  $\text{cm}^{-1}$  and that for  $\text{HF}^+$  is 326.8  $\text{cm}^{-1}$ . We have been able to improve our knowledge of several molecular parameters of  $\text{HF}^+$  from these observations, especially the spin-orbit coupling constant and the  $^{19}\text{F}$  hyperfine parameters. In addition, it is now possible to record low-frequency vibrational (usually bending) transitions of open shell molecules within this wavelength range. Some results on the quasi-linear species, HCCN in its ground  $^3A''$  state, will also be presented.

# Ionization of water molecule by metastable neon atoms

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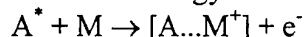
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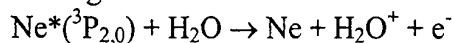
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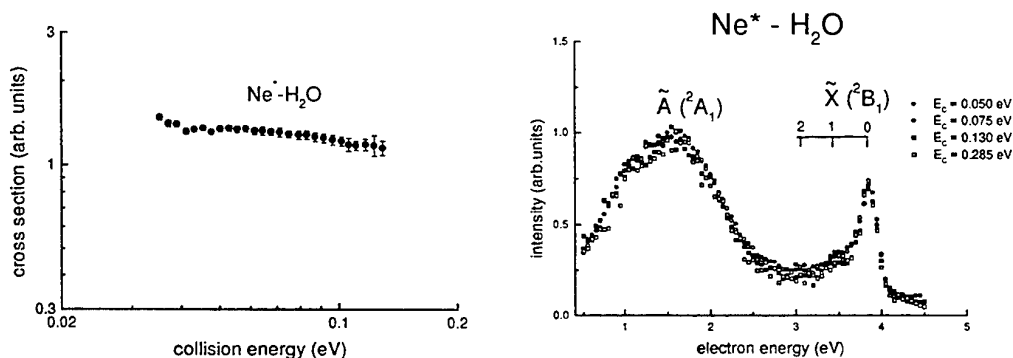
A molecule, M, can be ionized by collision with an excited atom,  $A^*$ , when the ionization potential of M is lower than the  $A^*$  excitation energy



The ionic complex  $[A...M^+]$  then continues the collision leading to the final ionic products. In the case of  $H_2O$  ionized by metastable neon atoms, the only ionization channel energetically possible is the Penning ionization:



The energy dependence of the ionization cross section and the energy distribution of the emitted electron have been measured in a crossed beam apparatus. In Fig.1 the ionization cross sections as measured in the collision energy range between 0.03 and 0.2 eV and the electron energy spectrum obtained at four different collision energies are shown.



**Fig. 1:** Ionization cross section and electron energy spectrum of the emitted electron for  $Ne^* - H_2O$  collisions.

The analysis of the energy distribution of product electrons in this type of autoionization process can provide very detailed information about the dynamics of the ionization event. Actually the electron leaves the system in a time short enough that it does not perturb the nuclear motion and consequently its energy reflects the state distribution of products. In the present case, two electronic states of the  $H_2O^+$  ion are accessible, the ground state  $\tilde{X}(^2B_1)$ , which is obtained by removing one electron from the lone-pair orbital perpendicular to the molecular plan, and the first excited  $\tilde{A}(^2A_1)$  state, obtained by removing one electron from the lone-pair orbital on the molecular plane.

An analysis of the experimental data in terms of potential energy curves has been started, and some results of such an interpretation will be given at the meeting.

# Electron spectroscopy study of the ionization in the $\text{Ne}^*(^3\text{P}_{2,0}) + \text{Kr}$ system

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The analysis of the energy distribution of product electrons in the autoionization process can provide very detailed information about the dynamics of the ionization event. Actually the electron leaves the system in a time short enough that it does not perturb the nuclear motion and consequently its energy reflects the state distribution of products. When interaction potentials in the neutral entrance and in the ionic exit is well known, electron energy spectroscopy, in atom-atom systems, can provide information about the effect of fine structure on the ionization efficiency.

The crossed beam apparatus for collisional autoionization studies, in operation in Perugia, has been recently implemented with a hemispherical electron energy analyzer that allows us to measure the energy distribution of product electrons for processes at different collision energies. The energy resolution has been determined by measuring the photoionization electron spectrum for some known systems.

The electron energy spectrum for  $\text{Ne}^*(^3\text{P}_{2,0}) + \text{Kr}$  obtained, with a resolution of  $\sim 40$  meV (FWHM), is shown in Figure 1. The contributions for the fine structure components, of the metastable reacting atom,  $^3\text{P}_2$  and  $^3\text{P}_0$ , and of the atomic ionic product,  $^2\text{P}_{1/2}$  and  $^2\text{P}_{3/2}$ , appear satisfactorily resolved.

The analysis of the spectra, which have been measured for different collision energies, are presently in progress and is based on a semiclassical calculation starting from the potential energy curves describing the interaction between the two neutral partners and those for the final ionic products. Some results of such analysis will be given at the meeting.

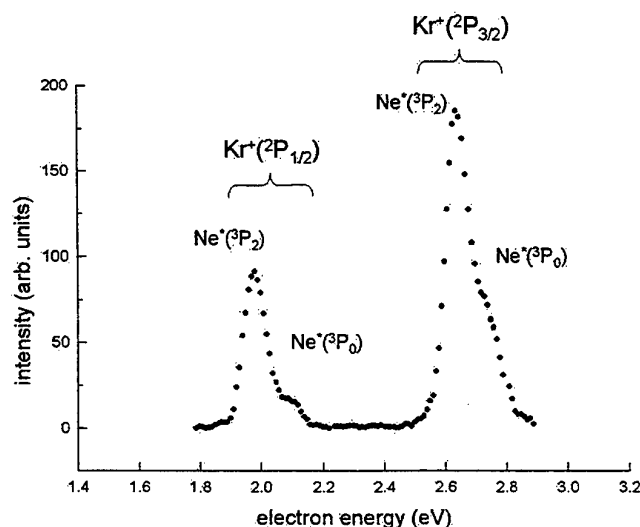


Fig.1: Electron energy spectrum for the collisional autoionization of krypton by metastable neon atoms at a collision energy of 50 meV.

# Atomic silicon chemistry at very low temperature : kinetic measurements on reactions of $\text{Si}(^3\text{P}_J)$ with $\text{O}_2$ , $\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_4$ at temperatures down to 15 K and interstellar consequences

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Silicon is one of the most abundant element in the Universe. Silicon-bearing molecules, however are found to be under-represented in the interstellar medium when compared to silicon cosmic abundance. So far the detected silicon containing molecules are SiO, SiS, SiC, c-SiC<sub>2</sub>, SiC<sub>4</sub>, SiH<sub>2</sub>, SiH<sub>4</sub>, SiC<sub>3</sub> and SiCN. This apparent under-representation could be explained by a lack of accurate spectroscopic data on silicon-bearing molecules, and also because atomic silicon, like other refractory elements, is known to be highly depleted from the gas phase due to its incorporation into silicate grains or into nanoparticles.

Very few silicon-containing molecules have been detected in dense molecular clouds as well as in Photon Dominated Regions where silicon is expected to be mainly in the form of SiO or SiS. Our kinetic measurements on  $\text{Si}(^3\text{P}_J) + \text{O}_2 \rightarrow \text{SiO} + \text{O}^1$  reaction show that this reaction is very fast even at very low temperature ( $k = 2.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 15 K) and confirm that most of the gas phase silicon is expected to be in the form of SiO in dark clouds and therefore cannot explain the low upper limit detection of SiO in dense clouds.

Silicon carbides and all relatively complex silicon bearing molecules (with the exception of silane) have been observed in the circumstellar envelope of the carbon-rich star IRC+10216, in which the temperature varies between 30 K (outer envelope) and 400 K (inner envelope). **Reactions of  $\text{Si}(^3\text{P}_J)$  with hydrocarbons ( $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$ )**<sup>2</sup> have been recently included in some models using "guessed" rate constants at low temperature, and our measurements are the first kinetic study at very low temperature (down to 15 K) for these two reactions.

This experimental work has been achieved at the **University of Rennes** using a **CRESU** (Cinétique de Réaction en Ecoulement Supersonique Uniforme) facility associated to the **PLP-LIF** (Pulsed Laser Photolysis – Laser Induced Fluorescence) technique. Silicon atoms were generated by multiphoton photolysis of  $\text{Si}(\text{CH}_3)_4$  using a 266 nm Nd:YAG laser mildly focused, and detected by LIF employing the ( $3p^2\ ^3\text{P}_0 - 4s\ ^3\text{P}_1$ ) transition of atomic silicon at 251.43 nm using a MOPO.

For the three reactions the rate constants are found to be fast ( $k > 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) at 300 K and to increase when the temperature is lowered.

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<sup>2</sup> A. Canosa, S.D. Le Picard, S. Gougeon, C. Rebrion-Rowe, D. Travers and B.R. Rowe, *J. Chem. Phys.*, submitted.

**Three-center atomic and radical reactions:  
hyperspherical elliptic coordinates and harmonic representations**

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The three body problem in particle, atomic and molecular physics has always been a fundamental task, because it is the simplest problem involving the rearrangement of the bodies, and the methods developed for its solution can be used for more general cases. The hyperspherical method has revealed itself as one of the most powerful tools for the study of reactive collisions, because it allows a separation of the hyperradial variable in a way very similar to the Born-Oppenheimer separation. The remaining part of the hamiltonian, the hyperangular part, needs to be parametrized correctly [1] [2] to exploit the physical features of the system while the reaction is going on and to achieve in this way suitable basis sets for the expansion of the hyperangular part of the wave function. The search of basis sets with better properties of convergence has lead us to elliptic sets, that can be expressed in terms of the Jacobi elliptic functions [3]. These sets have an additional parameter which can be suitably set for different situations, and gives more flexibility to the set, allowing, among other things, a smooth transition between asymmetrical and symmetrical parametrizations, and approximate separation of the two angular variables needed to parametrize the hypersphere in the  $J=0$  case. The choice of the parameter according to the reaction skewing angle has been shown to be succesful in particular cases [4]. Since these basis sets, that can be related to Lamé' polynomials, cannot be expressed in a closed form, they are calculated by expansions in spherical harmonics, by a three terms recurrence relation [5]. This fact produces both a simplification in the use of these sets, avoiding the use of complicate (and unsuitable for calculations) Jacobi functions and taking into account the eight classes of the Lamé' polynomials simply by the factorization of the expansion matrix in eight blocks. When considering the  $J>0$  case, we can exploit the partition of the hamiltonian first suggested by Launay and Ledourneuf (see also [6]) , and we can easily make a direct extension of our elliptic sets by using elliptic cylindrical coordinates on the sphere  $S_3$  to treat this more general case.

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## Dynamics of formation of $C_3H$ , $C_3H_3$ , and $C_4H_3$ radicals and of $C_3$ from crossed beam studies of the reactions of $C(^3P, ^1D)$ with unsaturated hydrocarbons ( $C_2H_2$ , $C_2H_4$ , $C_3H_4$ )

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In this contribution we report on the investigation of the dynamics of some important reactions of  $C(^3P, ^1D)$  with unsaturated hydrocarbons (acetylene, ethylene, and methylacetylene), a work carried out in a synergistic fashion with low temperature kinetic<sup>1</sup> and low energy dynamic (integral cross sections)<sup>2</sup> work within the EC Network on Astrophysical Chemistry. These reactions are of basic chemical interest and of great relevance in areas which range from combustion to astrochemistry. Kinetic studies of a variety of  $C(^3P)$  reactions with unsaturated hydrocarbons ( $C_2H_2$ ,  $C_2H_4$ ,  $C_3H_4$ , etc.) found them very fast ( $k \approx 2-4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) down to very low temperature (15 K) and suggested that these are barrierless reactions dominated by long range attractive forces and that may have a critical role in the chemistry of the ISM.<sup>1</sup> These studies, however, follow the decay of  $C(^3P)$  and do not provide information on the primary products and on the dynamics of the reaction.

From measurements of product angular and velocity distributions at different mass-to-charge ( $m/e$ ) ratios we have identified the primary products and determined their branching ratios for both  $C(^3P)$  and  $C(^1D)$  title reactions, have derived their angular and translational energy distributions in the CM frame, have characterized the reaction micromechanism, and have obtained information on the PESs governing the transformation from reactants to products.<sup>3</sup> The results can be summarized as follows. All three reactions,  $C(^3P, ^1D) + C_2H_2$ ,  $C_2H_4$ , and  $C_3H_4$ , are found to proceed through a strongly bound intermediate ( $C_3H_2$ ,  $C_3H_4$ , and  $C_4H_4$ , respectively) that lives a time comparable to its rotational period. Formation of  $H + H_2CCCH$  (propargyl) is the dominant pathway, at low collision energy ( $E_c$ ), of the  $C(^3P, ^1D) + C_2H_4$  reaction, while at high  $E_c$  formation of the less stable  $C_3H_3$  isomers (cyclopropenyl and/or propyn-1-yl) also occurs; the  $H_2$  elimination channel is negligible and no  $C(^1D)$  contribution has been observed. The  $H$  elimination channel has also been found to be the dominant pathway in the  $C(^3P, ^1D) + CH_3CCH$  reaction leading to  $C_4H_3$  isomers (both the triplet and singlet dynamics has been characterized); again, no  $H_2$  elimination was observed to occur. In contrast, both  $H$  and  $H_2$  elimination, leading in comparable ratio to  $C_3H + H$  and  $C_3(X^1\Sigma_g^+) + H_2(X^1\Sigma_g^+)$ , respectively, have been observed in the reaction  $C(^3P) + C_2H_2(X^1\Sigma_g^+)$  at a collision energy of  $E_c = 29.3 \text{ kJ/mol}$ . The dynamics of  $C_3H + H$  formation from  $C(^1D)$  has also been characterized. The occurrence of the spin-forbidden molecular pathway in the  $C(^3P) + C_2H_2$  reaction, never detected before,<sup>4</sup> has been rationalized by invoking the occurrence of inter-system-crossing between triplet and singlet manifolds of the  $C_3H_2$  PESs. These findings are supported by recent kinetic<sup>5</sup> and dynamic<sup>2</sup> experiments, as well as by theoretical calculations<sup>6</sup> and may have important consequences in establishing the role of this reaction in the modeling of combustion and interstellar chemistry networks. For all the reactions the dynamics are discussed in the light of recent theoretical calculations on the relevant potential energy surfaces.

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## Structure and Dynamics of Molecular Clusters Containing Hydrocarbons

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Recently (1) we experimentally demonstrate how a planar molecule tends to travel as a "frisbee" when as gaseous mixture with lighter carriers expands into a vacuum, the orientation being due to collisions. The molecule is benzene, the prototype of aromatic chemistry. The demonstration is via two complementary experiments: interrogating benzene by IR-laser light and controlling its orientation by selective scattering on rare-gas targets. The results cast new light on the microscopic mechanisms of collisional alignment (2) and suggest an useful way to produce intense beams of aligned molecules, permitting studies of steric effects in gas-phase processes. This study has been extended to other simple hydrocarbons such as ethylene, acetylene and ethane, indicating that collisional alignment is effective also in these cases.

In this communication we show that combining scattering studies of supersonic seeded beams of aligned molecules with results from scattering of rotationally hot molecular beam and together with the use of empirical methods for the calculation of intermolecular forces we are able to characterize the degree of molecular alignment in the beam and also the structure and dynamics of molecular cluster containing simple hydrocarbons, like the ones mentioned above, and rare gases.

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## INFRARED SPECTROSCOPY OF $C_2H_2$ -HCl AND $C_2H_4$ -HCl COMPLEXES

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The study of small molecular complexes leads to very accurate experimental data that can be supplemented by quantum chemistry calculation performed at high level of theory in order to have a comprehensive view of the system.

By means of an experimental setup composed of a pulsed slit jet and diode laser spectrometer we have observed the infrared absorption spectra in the 3.6  $\mu m$  region of the H-Cl stretching mode in the  $C_2H_2$ -H<sup>35</sup>Cl and  $C_2H_2$ -H<sup>37</sup>Cl complexes at low temperature (12 K) and high resolution ( $<5 \times 10^{-3}$ ). The spectrum of the  $C_2H_4$ -HCl complex has also been recorded with this experimental setup.

The spectral analysis of the  $C_2H_2$ -H<sup>35</sup>Cl and  $C_2H_2$ -H<sup>37</sup>Cl complexes have provided the rotational and centrifugal constants for the  $v = 0$  and  $v = 1$  vibrational states of the electronic ground state and the H-Cl vibrational frequency shifts due to complexation. The same information have been obtained from the analysis of the  $C_2H_4$ -HCl which is still in progress.

These experimental spectroscopic results on the H-Cl intramolecular vibration have been used in order to characterize the intermolecular bond with the pseudo-diatomic model.

In view of having a more extended understanding of the studied systems, we have performed *ab initio* calculation at the CCSD(T) level of theory with a cc-pVTZ basis set. An anharmonic potential for the intermolecular stretching mode has been calculated on a 2 dimensional grid. This calculation made possible to analyze independently the effects of anharmonicity, of Basis Set Superposition Error and of coupling between intra- and intermolecular motions on the calculated results for such molecular complexes.



## Vibronic Spectroscopy of Benzyl-type Radicals: Jet-Cooled Chlorobenzyl Radicals in the $D_1 \rightarrow D_0$ Transition

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One of the most interesting subjects in modern molecular spectroscopy is to determine the structure of transient species in the gas phase, since they are believed to play important roles in chemical reaction as intermediates. Among transient species, benzyl-type radicals have attracted much attention as being a useful candidate for diagnostics of the combustion process of aromatics.

Since chlorinated benzenes consist of the core parts in the structure of the highly toxic dioxin chemicals, the spectroscopic studies on the chlorobenzyl radicals could be useful for the understanding of formation process of dioxin in the exhaust gas of incinerator. To date, however, no one has reported the spectroscopic analysis of three chlorobenzyl radical isomers in the gas phase.

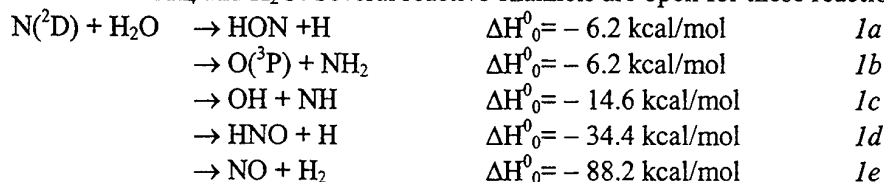
The chlorobenzyl radicals have been generated from chlorotoluenes seeded in a large amount of carrier gas He and vibronically excited in a corona excited supersonic expansion using a pinhole-type quartz nozzle which has been significantly improved in this laboratory. The vibronic emission spectra of jet cooled chlorobenzyl radicals in the  $D_1 \rightarrow D_0$  transition have been recorded with a long-path double monochromator equipped with a cooled PMT detector in the visible region. The observed spectra have been analyzed by comparing with the known vibrational data of corresponding precursors and the *ab initio* results calculated by using the GAUSSIAN 98 program to determine the accurate frequencies of vibrational modes as well as electronic transition.

## Crossed beam studies of the reactions $N(^2D)+H_2O$ and $N(^2D)+CH_4$ : Dynamics of formation of molecular and radical products

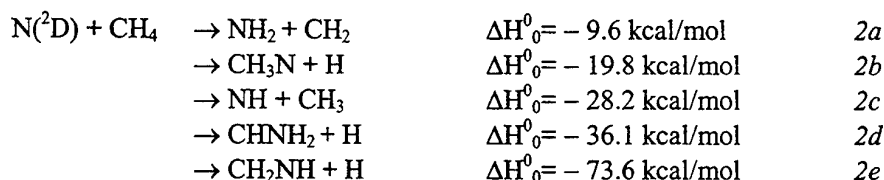
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The dynamics of  $N(^2D)$  reactions have recently become amenable to detailed experimental and theoretical<sup>2</sup> investigations. Nascent rovibrational distributions of the NH product from the reactions  $N(^2D)+H_2$ ,  $H_2O$ , and saturated hydrocarbons have been measured in pump-probe experiments.<sup>1</sup> The mechanism of the  $N(^2D)+H_2$ ,  $H_2O$ ,  $CH_4$ ,  $C_2H_2$ , and  $C_2H_4$  reactions have been theoretically investigated using *ab initio* molecular orbital theory.<sup>2</sup> We recall that  $N(^2D)$  reactions are of relevance in different environments, such as the upper terrestrial atmosphere and extraterrestrial environments.

We have undertaken reactive scattering studies of N atom reactions using the crossed molecular beam technique.<sup>3</sup> The reactions with  $H_2$ ,  $C_2H_2$ , and  $C_2H_4$  were first investigated.<sup>4</sup> Here we focus on the reactions with  $CH_4$  and  $H_2O$ . Several reactive channels are open for these reactions:



and



The channels which can be conveniently investigated by means of our experimental technique are those relative to H-displacement and  $H_2$ -elimination, that is channels 1a, 1d, and 1e from reaction 1 and channels 2b, 2d, and 2e from reaction 2.

In the case of the  $N(^2D)+H_2O$  reaction, we have measured product angular and velocity distributions at  $E_c=11.7$  and 7.3 kcal/mol; the isotopic variant  $N(^2D)+D_2O$  was also investigated at  $E_c=10.0$  kcal/mol.<sup>5</sup> We have established that the  $H_2$ -elimination channel is not open under our experimental conditions and that the H-displacement pathway actually occurs via two different channels, 1a and 1d, in the case of the high  $E_c$  experiments, while only channel 1d is open at  $E_c=7.3$  kcal/mol. The results are consistent with the *ab initio* information available on the PES of  $H_2NO$ .<sup>2,6</sup>

For  $N(^2D)+CH_4$ , we have measured product angular and velocity distributions at six different  $E_c$ , ranging from 5 to 15 kcal/mol.<sup>5</sup> We got evidence that two different mechanisms, one associated to channel 2b and one associated to channel 2e, are involved. They contribute differently to the observed signal and their relative importance is found to change considerably with  $E_c$ . The results are consistent with the reactive pathways recently described by an *ab initio* study of the relative PES.<sup>7</sup>

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## **Tropospheric Measurements from the ESA GOME Instrument: Boundary Layer HCHO and NO<sub>2</sub>**

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### **Abstract**

The ESA Global Ozone Monitoring Experiment (GOME) has been measuring ultraviolet and visible spectra of the Earth's atmosphere in the nadir geometry since April, 1995. Although the GOME mission objectives emphasized column ozone measurements, it was also realized that GOME could successfully measure important tropospheric species, including O<sub>3</sub>, HCHO, and SO<sub>2</sub> from volcanic sources (tropospheric BrO was not anticipated, but has become a robust product in polar springtime conditions).

Emission sources of HCHO can be clearly identified from GOME measurements, and quantified, subject to modeled radiative transfer constraints on the atmospheric seeing and vertical distribution. Tropospheric NO<sub>2</sub> can be distinguished from stratospheric NO<sub>2</sub> by spatial discrimination, and then quantified subject to similar constraints as for HCHO. Examples of measurements of these gases, including HCHO over the North American continent and the Amazon basin, and world-wide distribution of NO<sub>2</sub>, are presented and compared with modeled distribution from the GEOS-CHEM 3-D tropospheric chemistry and transport model.

## A High Resolution Spectroscopic and Computational Study of a Number of Alkoxy Radicals

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Alkoxy radicals are important intermediates in the oxidation of hydrocarbons both in combustion environments and the atmosphere. While the importance of these radicals is known, the spectroscopy of all but the smallest alkoxy radicals is almost unknown. Understanding the spectroscopy of these radicals is a prerequisite to doing experiments on the kinetics or dynamics of these important chemical intermediates. Such experiments could yield valuable information about specific reaction pathways and product information.

The spectroscopy of a few smaller alkoxy radicals (i.e. methoxy, ethoxy, 2-propoxy) has been quite well known for a number of years. Larger alkoxy radicals ( $\geq 4$  carbon atoms) have only recently been detected by laser induced fluorescence, with most of these experiments at or near room temperature. Most notably Dibble and co-workers have observed fluorescence from 2 butoxy isomers and 2 pentoxy isomers.

We have recently obtained vibronically resolved, jet-cooled spectra, of over 20 different alkoxy species. This includes radicals containing from 3 to 12 carbon atoms. In particular we did a detailed study of the 1- and 2- alkoxy radicals from 3-10 carbon atoms. All of the observed transitions lie in the near UV region of the spectrum.

These vibronically resolved spectra have many interesting characteristics, such as the origin frequencies being dependent on the branching of the hydrocarbon chain. Another interesting feature is the simplification of the spectra with increasing alkoxy radical size. Additionally we have found evidence of different conformers, even though they are not energetically favored, in the cold environment of the supersonic jet.

To answer some of the above questions we have initiated high resolution, rotationally resolved, studies of a number of the vibronic bands observed. These experiments are done with a laser linewidth of  $\sim 250$  MHz which is sufficient to resolve the rotational and spin-rotational structure. This resolution should suffice to determine which conformers are present in the spectrum even for the largest of the alkoxy radicals that we have observed.

As an aid to the analysis of the complex rotational structure observed, as well as a guide for the possible conformers that we might observe in these spectra, we have performed a number of *ab initio* calculations. In particular we have calculated all the possible conformers of the 1- and 2-pentoxy species as well as selective conformers of a number of the other alkoxy radicals.

Results of the rotational analyses will be compared with the calculated *ab initio* rotational constants. Analyses of the different conformers observed in the jet will be shown, as well as comparisons between the 1- and 2-alkoxy radicals.

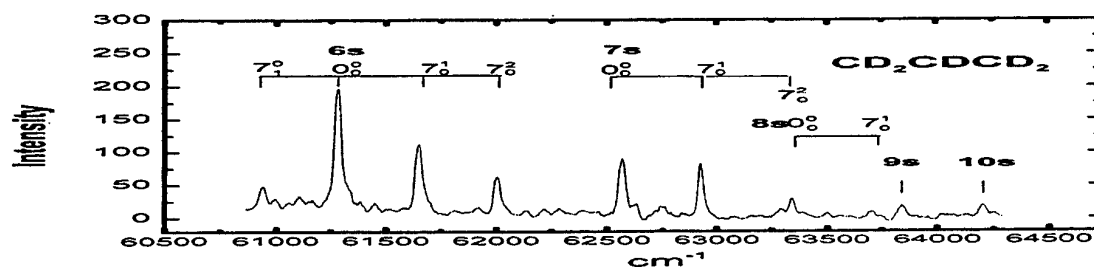
## Two-photon resonant ionization spectroscopy of the allyl-h<sub>5</sub> and allyl-d<sub>5</sub> radicals: Rydberg states and ionization energies

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The vibronic spectra of allyl-h<sub>5</sub> (CH<sub>2</sub>CHCH<sub>2</sub>) and allyl-d<sub>5</sub> (CD<sub>2</sub>CD<sub>2</sub>CD<sub>2</sub>) radicals at 6–8.2 eV have been observed using 2+1 resonance-enhanced multiphoton ionization (REMPI) spectroscopy. The allyl radicals were produced in the nozzle of a supersonic jet expansion by the pyrolysis of CH<sub>2</sub>CHCH<sub>2</sub>I and CD<sub>2</sub>CD<sub>2</sub>CD<sub>2</sub>Br. Rydberg states of ns (n = 4–11) for allyl-h<sub>5</sub> and (n = 4–10) for allyl-d<sub>5</sub> have been observed in the REMPI spectra (part of them shown below). Prominent vibrational progressions with the spacings of ~440 cm<sup>-1</sup> in allyl-h<sub>5</sub> and ~360 cm<sup>-1</sup> in allyl-d<sub>5</sub> are observed in the s Rydberg series. The totally symmetric ∠CCC-bending (ν<sub>7</sub>) is responsible for the observed vibrational progressions. Facilitated with *ab initio* calculated Franck-Condon factors, other vibrations (CH<sub>2</sub> rocking and C<sub>3</sub> stretching) observed in the s Rydberg series have also been identified. The term values for the ns (n = 6–11) Rydberg series of allyl-h<sub>5</sub> converge to an adiabatic ionization energy (IE) of 65585 ± 2 cm<sup>-1</sup> (8.1315 ± 0.0002 eV) with a quantum defect of δ = 0.917 ± 0.002. For allyl-d<sub>5</sub>, the fitting of the ns (n = 6–10) Rydberg series to Rydberg formula yields IE = 65526 ± 5 cm<sup>-1</sup> (8.1242 ± 0.0006 eV) and δ = 0.913 ± 0.005.

In our previous study,<sup>1</sup> IE = 65638 ± 18 cm<sup>-1</sup> for allyl-h<sub>5</sub> was obtained from the convergence of the ns (n = 4, 6–8) Rydberg states. This overestimated IE value (53 cm<sup>-1</sup>) in the fitting is due to the inclusion of the low-lying (likely perturbed) 4s Rydberg state, where penetration of the s electrons to molecular core usually causes sizable deviation from the Rydberg formula. In comparison with the recently determined IE = 65762 cm<sup>-1</sup> of allyl-h<sub>5</sub> using 1+1' ZEKE spectroscopy by Gilbert *et al.*,<sup>2</sup> we propose an interpretation for the discrepancy (177 cm<sup>-1</sup>) between the two IE values. In the overlapping area of the  $\tilde{B}$  and  $\tilde{C}$  states of allyl radical, which were chosen as intermediates in the 1+1' ZEKE experiment, an isomerization from allyl to cyclopropyl radical was reported.<sup>3</sup> Owing to the isomerization, the zero-point vibration of the allyl cation could be unreachable in the 1+1' ZEKE transitions, because of poor Franck-Condon overlap between the two dramatically displaced oscillators (C<sub>3</sub>H<sub>5</sub>,  $\tilde{B}, \tilde{C} \rightarrow \text{C}_3\text{H}_5^+, \tilde{X}$ ). Further spectroscopic investigation to the isomerization between allyl and cyclopropyl radicals is called for in future.



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## **Cavity enhanced absorption spectroscopy using a cw tunable diode laser and an optical cavity with ultra high reflectivity mirrors**

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An improved method for cavity enhanced absorption spectroscopy (CEAS) using a cw diode laser and an optical cavity with ultra-high reflectivity mirrors is described. The optical cavity consists of two mirrors ( $R > 99.9945\%$ ) separated at a distance of 60 cm, and was scanned by controlling a piezoelectric translator mounted on one of the mirrors at a rate of 3Hz. Laser radiation of 1.5  $\mu\text{m}$  from a tunable narrow linewidth cw diode laser was coupled into the optical cavity, and scanned at a rate of  $1.6 \times 10^{-3} \text{ cm}^{-1}/\text{s}$ . Cavity enhance absorption information was extracted by recording the maximum transmission amplitudes at each datum point. A wavemeter was used simultaneously to record accurate wavelength of the laser. A noise-limited absorbance sensitivity about  $1 \times 10^{-9} \text{ cm}^{-1}$  has been achieved. Absorption spectra of vibrational combination bands of  $\text{CO}_2$  in the 1.5  $\mu\text{m}$  region have been obtained. In addition to the transition lines that are listed in the HITRAN database, we have recorded some new lines of  $\text{CO}_2$  in this region that have not been reported.

**Acknowledgement:** The work was carried out with support from the Hong Kong Research Grants Council under Grant no. HKU 7138/99P

## INELASTIC COLLISIONS OF ORIENTED OH RADICALS

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In addition to the velocities and to the initial internal state distributions of the collision partners, the relative orientation is a determining factor for the outcome of the scattering process. The measurements of the steric effects in inelastic and reactive scattering provide detailed information about the interaction potential and consequently, represent a test for the *ab-initio* potentials.

An electrical discharge produced at the valve exit followed by a supersonic expansion was used to prepare rotationally and vibrationally cooled OH ( $X^2\Pi$ ) radicals. An electrostatic hexapole was used to focus in the collision center only the radicals in the  $J=3/2$ ,  $M_J=3/2$ ,  $f$  state. In order to measure the steric dependence, the OH radicals were oriented by means of a static field applied in the collision region. By switching the direction of the electric field, the radicals were oriented with the O- or H-side towards the collision partners. Saturated LIF spectroscopy of  $A^2\Sigma^+-X^2\Pi$  transition of the OH radical was used to determine relative state-to-state cross sections. For Ar as a collision partner, the high (up to 78%) values obtained for the steric factors indicate a high preference for the collisions at the H-side, the excitation cross section in this case being 8.1 times larger than the cross section for collision at the O-side. The same type of behaviour was exhibited in collisions of OH with the diatomic molecules  $N_2$  and CO. At the moment we are performing inelastic scattering experiments on a new 4-atom system OH + HCl.

In this presentation we describe the experimental technique used to perform state-to-state collisions in crossed molecular beams experiments with oriented OH radicals. The results obtained for the relative total integral cross sections and steric asymmetry dependence are presented for the inelastic scattering of the OH with its collision partners.

## Air Broadened Linewidths of Some Atmospheric Free Radical Rotational Transitions

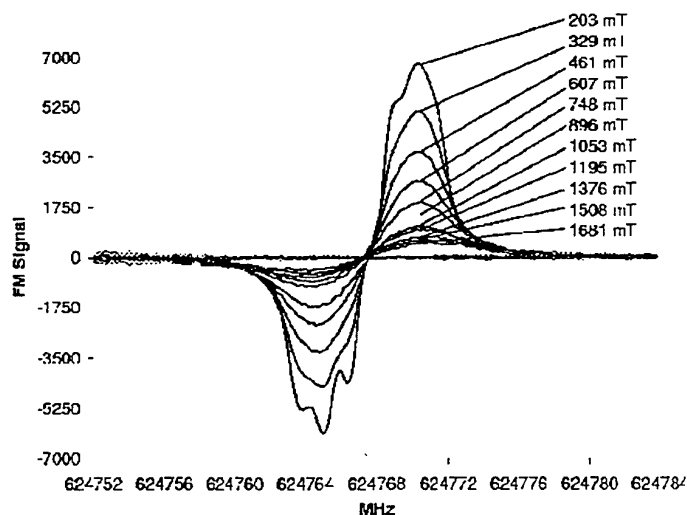
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The AURA-MLS microwave limb sounding spectrometer will observe atmospheric trace gases from orbit with several radiometers. In support of this mission, the pressure and temperature dependence of the broadening and shift parameters for a variety of species must be measured and/or improved. This presentation will focus on recent measurements in the 600 GHz region.

The radical species BrO has several transitions in the detection window, and is expected to be measurable over long integration times. Since there are no published data on the pressure and temperature dependence of the bromine oxide lineshape, a systematic study of several different rotational transitions was begun. Similar measurements of another radical species, HO<sub>2</sub>, crucial to understanding the HO<sub>x</sub> cycles of the stratosphere, are in progress. These will be compared with earlier measurements of the ClO radical.<sup>1</sup>

Laboratory measurements utilize directly synthesized radiation produced through successive multiplication of a frequency synthesizer, pumping an active sextupler followed by a passive anti-parallel planar Schottky multiplier to generate the 500-700 GHz radiation. A free-space cell equipped with a methanol-cooled jacket is employed to determine the lineshape dependence upon nitrogen/oxygen pressure and temperature in the 0.2 mbar - 3.0 mbar and 208 - 300 K ranges. Measurements are planned for other species, including OH up to 2.5 THz. These will utilize a difference frequency spectrometer.<sup>2</sup>



A room temperature run of BrO in Oxygen.

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<sup>2</sup> S. Matsuura, P. Chen, G. A. Blake, J. C. Pearson, and H. M. Pickett, *IEEE T. Microw. Theory*, **48**, 380-387 (2000).



# HIGH RESOLUTION FOURIER TRANSFORM MEASUREMENTS OF THE NO<sub>2</sub> ABSORPTION CROSS-SECTION IN THE NEAR-IR AND VISIBLE REGIONS: TEMPERATURE AND PRESSURE EFFECTS.

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The NO<sub>2</sub> radical plays an important role in atmospheric chemistry. Its detection, either in the troposphere or in the stratosphere, is based on spectroscopic techniques, which require the knowledge of accurate absorption cross-sections. These cross-sections need to be obtained under temperature and pressure conditions close to the ones prevailing in the atmosphere.

In one of our previous studies [1] it was shown that laboratory spectra of atmospheric molecules need to be recorded at a high enough resolution so that all the absorption features are fully resolved. This is the case for the NO<sub>2</sub> radical, which exhibits resolved structures in the visible region that are commonly used for its stratospheric detection. In [2] a pressure effect on the NO<sub>2</sub> absorption cross section was observed, but could not be quantified. In order to study this effect, high resolution must be used. It is also widely acknowledged that the temperature dependence of the absorption cross-section of NO<sub>2</sub> must also be taken into consideration when measuring stratospheric concentrations

The absorption cross-section of NO<sub>2</sub> has therefore been re-investigated at resolutions of 0.05 and 0.1 cm<sup>-1</sup> in the range of 11000 to 25000 cm<sup>-1</sup>. Measurements have been performed under various conditions of pressure (pure NO<sub>2</sub>, NO<sub>2</sub> diluted in a mixture of N<sub>2</sub>+O<sub>2</sub> with dilutions of 9.6 ppm, 92 ppm, and 965 ppm), and at three temperatures (293K, 240K, and 220K). The measurements were carried out with a Fourier transform spectrometer coupled to a 5m base multiple reflection temperature stabilized cell.

In this paper we will present results of measurements that will examine the effects of the temperature and of the pressure on the absorption cross-section of NO<sub>2</sub>.

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MOLECULAR CONSTANTS, POTENTIAL CURVE AND BORN-OPPENHEIMER  
BREAKDOWN CORRECTION FUNCTIONS FOR  $X^2\Sigma^+$  STATE OF BeH, BeD AND BeT

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The data for the  $A^2\Pi - X^2\Sigma^+$  and  $C^2\Sigma^+ - X^2\Sigma^+$  electronic transitions of BeH, BeD and BeT measured by Fourier transform spectroscopy<sup>a,b</sup> and by traditional methods<sup>c</sup> were combined to derive a ground state potential energy curve. In order to avoid the complication of perturbations in the excited states, the data were re-arranged and converted into fluorescence series into the ground state (method of Aslund). Two types of combined isotopomer fits were carried out. First a Dunham-type of expansion including corrections for the breakdown of the Born-Oppenheimer approximation was used for the ground state. An equally good fit was also obtained by using an analytical ground state model potential with adjustable parameters. In both cases the energy levels in the two excited states were fitted as term values. The potential function has the "MLJ" form<sup>d</sup> and was constrained to have the correct  $C_6/R^6$  long-range behaviour.

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Dynamics of C-H and C-C Bond Activation in Neutral Transition Metal Atom  
- Hydrocarbon Reactions

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The reactions of neutral transition metal atoms with hydrocarbons usually involve initial formation of reaction intermediates, often following C-H or C-C bond insertion. Unimolecular reactions of such intermediates may proceed via several competing pathways such as hydrogen atom loss, molecular hydrogen or ethylene elimination, or decay back to reactants. Using the method of crossed molecular beams with VUV photoionization of neutral products, we have measured product angular and velocity distributions from such reactions at well-defined collision energies. These measurements provide insight into the nature of the potential energy surfaces for C-H and C-C bond activation in model systems involving second row transition metal species.

SELECTIVE PRODUCTS FORMATION IN THE MOLECULAR BROMINE  
ELECTRONIC PREDISSOCIATION VIA MONOCHROMATIC ULTRA-SHORT  
LASER PULSES

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Interacting states in dissociative systems are commonly related to electronic predissociation. The interaction between the states involved, determine important aspects such as: the products branching ratios, the resonance widths, positions and life-time, observed in the photodissociation spectra. In the laser induced dissociation of many dihalogen molecules, the crossing of the interacting states most commonly acts breaking the selectivity which can be easily achieved in the Franck-Condon region. Several different theoretical schemes have been proposed to control reaction yields. However, most of them are related to a final products branching ratio which reflects equivalent quantities of population in the exit channels, corresponding to a low level of selectivity in the asymptotic region. In the present work, we use the wave packet formalism in the time dependent Fourier method to simulate the predissociation dynamics of molecular bromine. We employed femtosecond monochromatic laser pulses of Gaussian shape, with field strength  $\varepsilon_0 = 5 \times 10^{-5} \text{ a.u.}$  and width of 24 femtoseconds. Excitations in the frequency range of 0,08-0,074 a.u. produced a good selectivity in the  $\text{Br}/\text{Br}+\text{Br}^*$  branching ratio. Franck-Condon integrals, photodissociation cross-sections and auto-correlation functions were obtained in order to a detailed description of the dynamics.

## The A+BC reaction by the Hyperquantization Algorithm: open-shell, spin-orbit and long-range effects

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Within the framework of the hyperspherical approach to reaction dynamics [1], we have developed a method, *hyperquantization algorithm* [2] to solve exactly the quantum mechanical reactive scattering problem using as a basis generalized 3j symbols or Hahn Polynomials [3] as the discrete analogs of hyperspherical harmonics on a grid of points. The implementation of two different sequential diagonalization-truncation techniques [4] to diagonalize the Hamiltonian matrix makes this method efficient and competitive. Cross sections have been calculated for the prototype ion-molecule reaction  $\text{He} + \text{H}_2^+ \rightarrow \text{HeH}^+ + \text{H}$ , for which a new ab-initio surface has been proposed [5], and for the benchmark system  $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$ , for which the effects of the long-range and spin-orbit interactions have been studied.

The treatment is extended to excited electronic states for the  $\text{F} + \text{H}_2$  reaction, where the three surfaces accessible at thermal energies (1 A', 2 A' and A'') have been coupled by spin-orbit interaction [6]. Under this approach, the total angular momentum exhibits contributions from both nuclear and electronic motion, so that, owing to the electronic spin, possible values of the total momentum J are half-integer. The excited surfaces and the long-range behaviour of the interaction have been obtained from the analysis of scattering experiments [7].

We have obtained: (i) differential cross sections, allowing comparison with the experiments of Lee and co-workers; (ii) product rotational distributions, in agreement with recent measurements from Nesbitt and collaborators; (iii) energy dependence of total cross sections, which from the analysis of Liu's experiments indicates need for revised transition state for this reaction. Calculations on the Stark-Werner surface have been performed and compared with Castillo-Manolopoulos 'exact' results to check the accuracy of our methodology.

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## STANDARD ON-LINE REFERENCE SOURCE FOR OH LIF MEASUREMENT BY A PULSED LOW PRESSURE RF DISCHARGE

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The detection of OH is a crucial but difficult issue in atmospheric research. To this end techniques based on the Laser Induced Fluorescence (LIF) have been largely employed [1]. One of the problems of such techniques is their calibration, i.e. the disposal of a well-characterised source of OH for the calibration of the LIF outcome. In this contribution we propose a  $N_2$ - $H_2O$  low-pressure, low-power pulsed RF discharge as a calibrated source of OH. The quantitative determination of OH density comes from the demonstration achieved in [2] that  $OH(A^2\Sigma^+)$  and  $NO(A^2\Sigma^+)$  states excitation have the same precursor, the nitrogen triplet metastable  $N_2(A^3\Sigma_u^+)$ , in this kind of discharges. Therefore the OH density can be quantitatively correlated to the NO density through the intensity ratio of  $OH(A^2\Sigma^+)$  and  $NO(A^2\Sigma^+)$  emissions (the (0,0) band of the 3064 Å system and the  $\gamma$ -band system respectively). The OH density can then be measured by the measurement of NO density, that is much easier since NO is a stable specie.

We then demonstrate a LIF scheme by which OH and NO can be detected simultaneously by the use of one laser only, in which OH and NO are detected by the second and third harmonic respectively of the same dye laser output.

Finally we propose a discharge-LIF scheme that can be used as a standard on-line reference for atmospheric OH LIF monitoring. The proposed apparatus is composed by a pulsed-discharge reactor plus a NO reference cell. The best procedure requires the simultaneous detection of:

- 1- the LIF from OH and NO in the post-discharge,
- 2- the LIF from NO in the cell
- 3- the post-discharge emission from the (0,0) band of the OH 3064 Å system and from one of the NO  $\gamma$ -system bands.

By such a way an on-line OH density reference source can be built providing a reliable real-time calibration that is intrinsically robust with respect to:

1. variations of the production of OH and NO in the discharge;
2. laser energy drifts, i.e. it is not necessary to monitor the laser energy and to correct for its fluctuations according to *ad hoc* saturation curves;
3. laser wavelength drifts, i.e. complex devices for wavelength stabilisation can be avoided. A simpler device can be provided if a stable discharge, producing constant OH and NO quantities, can be set up and standardised by the previous scheme.

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## Ion-ligand Interactions of Biological Interest

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Ion-ligand interactions play a central role for many important biophysical phenomena (e.g., protein folding, molecular recognition), because of their much larger strength and longer range compared to neutral-neutral interactions. Despite of their importance, ion-ligand dimers are spectroscopically far less characterized than their neutral counterparts [1]. In this contribution we present the first (IR) spectroscopic and ab initio data for two important prototype systems which display a broad range of ion-ligand binding types: the phenol-Ar and the benzene-water cations ( $\text{Ph}^+\text{-Ar}$  and  $\text{Bz}^+\text{-H}_2\text{O}$ ). IR spectra of both species are obtained by photodissociation in a tandem mass spectrometer. The cluster ions are produced in a molecular beam combined with electron impact ionization (EI).

**$\text{Ph}^+\text{-Ar}$ :** Ph offers several competing ligand binding sites, such as H-bonds to the OH group and  $\pi$ -bonds to the  $\pi$ -electron system of the aromatic ring. In neutral Ph-Ar, dispersion forces prefer the formation of a  $\pi$ -bond over a H-bond. However, the situation is reversed in  $\text{Ph}^+\text{-Ar}$ , as induction dominates the attraction in the cation. H-bonded  $\text{Ph}^+\text{-Ar}$  is the first example of an aromatic-Rg complex in which the rare gas (Rg) ligand does not prefer  $\pi$ -bonding to the aromatic ring [2].

**$\text{Bz}^+(\text{H}_2\text{O})_n$ :** Neutral Bz-H<sub>2</sub>O represents a prototype aromatic-hydrophilic interaction and features a well studied  $\pi$  H-bond. In contrast, the  $\text{Bz}^+\text{-H}_2\text{O}$  cation is not characterized at all, although the interaction between an aromatic hydrocarbon cation and water is very important for biophysical processes. The first spectra of  $\text{Bz}^+(\text{H}_2\text{O})_n$  clusters reveal detailed information about both the dimer interaction and the  $\text{Bz}^+$  microhydration process. The dimer has an intriguing charge-dipole structure in which the oxygen atom of H<sub>2</sub>O approaches the  $\text{C}_6\text{H}_6^+$  cation in the aromatic plane to form hydrogen bonds with two protons of  $\text{C}_6\text{H}_6^+$ . The dissociation energy estimated from the spectral shifts,  $D_0 \approx 14 \pm 3$  kcal/mol, is in good agreement with theoretical results. The spectra of larger  $\text{Bz}^+(\text{H}_2\text{O})_n$  complexes indicate two competing routes for cluster growth: formation of a water network and hydration of the  $\text{Bz}^+$  cation.

Both examples show the dramatic changes of the interaction induced by ionization. This is the reason why methods using resonance enhanced multiphoton ionisation (REMPI) of the neutral precursor in molecular beams fail to produce cold cluster ions for subsequent spectroscopic interrogation. In contrast, our EI ion source appears more generally applicable to cluster ion spectroscopy.

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**Intermolecular interaction, hindered internal rotation, and  
microsolvation in open-shell ionic complexes:  $\text{NH}_3^+\text{-Ar}_n$  ( $n=1\text{-}6$ )**

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The intermolecular interaction and microsolvation process of ground state  $\text{NH}_3^+$  ( $D_{3h}$ ,  $^2A_2''$ ) in argon are studied by infrared photodissociation spectroscopy of isolated  $\text{NH}_3^+\text{-Ar}_n$  complexes ( $n=1\text{-}6$ ) in a tandem mass spectrometer and ab initio calculations.

**$\text{NH}_3^+\text{-Ar}$ :** Analysis of the rovibrational structure of the dimer spectrum yields a planar proton bound equilibrium structure with  $C_{2v}$  symmetry, an intermolecular N-Ar separation of 3.28 Å and an intermolecular stretching force constant of 11.14 N/m. These observations are in excellent agreement with ab initio calculations at the MP2/aug-cc-pVTZ level which predict a dissociation energy of 1100  $\text{cm}^{-1}$ . Observed tunneling splittings are attributed to hindered internal rotation of the planar  $\text{NH}_3^+$  cation within the dimer. The barrier for this hindered motion between the three equivalent proton bound minima amounts to 300  $\text{cm}^{-1}$ .

Comparison with the related systems  $\text{NH}_2^+\text{-Ar}$ ,  $\text{NH}_4^+\text{-Ar}$ ,  $\text{CH}_3^+\text{-Ar}$  and  $\text{OH}_3^+\text{-Ar}$  provides insight into the interaction potential and the reactivity of the respective molecular ion as a function of the number of protons and the electron density in the  $2p_z$  orbital of the central atom. Ab initio calculations support the interpretation of the experimental data.

**$\text{NH}_3^+\text{-Ar}_n$  ( $n>1$ ):** Systematic frequency shifts observed in the spectra of larger clusters provide a detailed picture of the cluster growth. The first three Ar ligands form equivalent linear proton bonds, leading to highly symmetric cluster structures with  $C_{2v}$  or  $D_{3h}$  symmetry. The next two Ar atoms bind to the partially filled  $2p_z$  orbital of the central N atom on opposite sites of the  $C_3$  axis, leading to structures with  $C_{3v}$  and  $D_{3h}$  symmetry. The ion-ligand induction interactions are highly non additive and non cooperative, i.e., the ligand binding energies decrease as a function of increasing solvation.

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Resonances in three-body reactions studied by a full angular momentum, smooth exterior complex scaling finite element method.

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A report in Science Magazine <sup>1</sup> last year highlights two recent experiments involving the *HDH* <sup>2</sup> and the *FHD* <sup>3</sup> reaction complexes. Both of these cited studies give, for the first time, *evidence of resonances as intermediate products in chemical reactions*. Both cited reports contain theoretical analysis that support the respective experimental discoveries. However, none of the cited studies use direct theoretical methods to compute the resonances. Instead, these studies are based on quantum scattering theory. We have during the passed ten years devepoled a method which computes complex eigenenergies and eigenfuctions for general, so far single potential surface, three-body systems. The method has been applied to bound states in the two isotopic antiprotomic helium systems ( $\bar{p}-^4\text{He}^{2+}-e^-$  and  $\bar{p}-^3\text{He}^{2+}-e^-$ ) to predict transition energies to an accuracy of a few ppm relative to experiment<sup>4</sup>. Eigenenergies and autoionization rates have been computed for *S*, *P* and *D* states of doubly excited helium<sup>5</sup>. Having tested our formalism and code on the two coulomb interacting systems we were ready to attack a model of predissociating triatomic molecule. Recently we reported the first fully quantum mechanical calculation of predissociation widths for a triatomic molecule - a model of the *NeICl* van der Waals complex<sup>6</sup>. Using this experience we have recently undertaken a study of the resonances discussed by Skodje et al.<sup>3</sup> for the *FHD* transition state. While Skodje et al.<sup>3</sup> discuss **one resonance** with an energy of about 200 inverse centimeters and a width of 48 inverse centimeters we find **two close lying resonances** in the interesting energy region. We have used an approximate formulation of a Laurent expansion of the *S*-matrix<sup>7</sup> to compute a folded resonance profile. This profile agrees with the single resonance profile of Skodje et al.<sup>3</sup>

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PHOTOINDUCED REDUCTION OF QUINONES WITH ALKYLAROMATICS.  
COMPETITION BETWEEN THE DECAY CHANNELS OF RADICAL IONS

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Upon light absorption, quinones are known to give fast intersystem crossing to populate the lowest excited triplet state ( $T_1$ ), a species which can decay either by a H-atom transfer process or by an electron transfer process with formation of the corresponding radical ions. The reactivity of these radical ions is of great interest because these intermediates are involved in photoinduced processes of biological and industrial interest. Generally, when the substrate is an alkylaromatic compound, being the corresponding radical cation a strong carbon acid, the heterolytic cleavage of the C-H bond in side-chain occurs.[1] The occurrence of a homolytic cleavage of the same C-H bond was recently observed in the photoinduced electron transfer reactions of  $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$  and aryl alkyl sulfides sensitized by chloranil (CA).[2] In this context, it appeared interesting to investigate this process in more details, by also changing the molecular structure of the photosensitizer.

This study deals with the investigation of the reactivity of the cation radical of  $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$  photosensitized by different quinines (Q) in acetonitrile. The main photoreaction products were  $(4\text{-MeOC}_6\text{H}_4)_2\text{CHOC}_6\text{H}_4\text{OH}$ ,  $(4\text{-MeOC}_6\text{H}_4)_2\text{CHCl}$  and  $(4\text{-MeOC}_6\text{H}_4)_2\text{CHOH}$ , depending on the nature of Q. The transient species (radical ions, neutral radicals, and ions) were detected and characterized by laser flash photolysis. The radical ions produced by interaction between the triplet quinone (Q) and  $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2$  mainly decay by back electron transfer process, but low efficient reactive channels for  $Q^{\bullet-}$  and  $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}_2^{\bullet+}$  were also (1) the proton transfer process and (2) the hydrogen transfer process. Quantum mechanical calculations with the model B3LYP/6-311G(d,p) suggest that the reactivity of the radical ions are mainly determined by the Mulliken charges on the oxygen atom of  $Q^{\bullet-}$ . Spin densities seem to be much less important.

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**Polarized Infrared Absorption Spectrum of Matrix-Isolated  
Methylperoxyl Radicals,  $\text{CH}_3\text{OO } \tilde{X}^2\text{A}''$**

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We have used a tandem pair of supersonic nozzles to produce clean samples of  $\text{CH}_3\text{OO}$  radicals in cryogenic matrices. One hyperthermal nozzle decomposes  $\text{CH}_3\text{NNCH}_3$  to generate intense pulses of  $\text{CH}_3$  radicals while the second nozzle alternately fires a burst of  $\text{O}_2/\text{Ar}$  at the 20 K matrix. The  $\text{CH}_3/\text{O}_2$  radical sandwich reacts to produce target methylperoxyl radicals. The absorption spectra of the radicals are monitored with a Fourier Transform infrared spectrometer. We report 10 of the 12 infrared bands of the methylperoxyl radical  $\text{CH}_3\text{OO } \tilde{X}^2\text{A}''$ , in an argon matrix at 20 K. The experimental frequencies ( $\text{cm}^{-1}$ ) and polarizations follow. The  $a'$  modes: 3032, 2957, 1448, 1410, 1180, 1109, 902, 492 and  $a''$  modes: 3024 and 1434. We do not detect the asymmetric  $\text{CH}_3$  rocking mode,  $\nu_{11}$ , nor the torsion,  $\nu_{12}$ . The infrared spectra of  $\text{CH}_3^{18}\text{O}^{18}\text{O}$ ,  $^{13}\text{CH}_3\text{OO}$ , and  $\text{CD}_3\text{OO}$  have been measured as well in order to determine the isotopic shifts. The experimental frequencies,  $\{\nu\}_i$ , for the methylperoxyl radicals are compared to harmonic frequencies,  $\{\omega\}_i$ , resulting from an DFT electronic structure calculations [UB3LYP/6-311G(d,p)]. Linear dichroism spectra were measured with photo-oriented radical samples in order to establish the experimental polarizations of most vibrational bands. True gas-phase vibrational frequencies of the methylperoxyl radicals were estimated by considering the gas-to-matrix shifts. The methylperoxyl radical matrix frequencies listed above are within  $\pm 1\%$  of the gas phase vibrational frequencies.

# TRAJECTORY STUDIES OF CHEMICAL REACTIONS USING BOND ORDER COORDINATES

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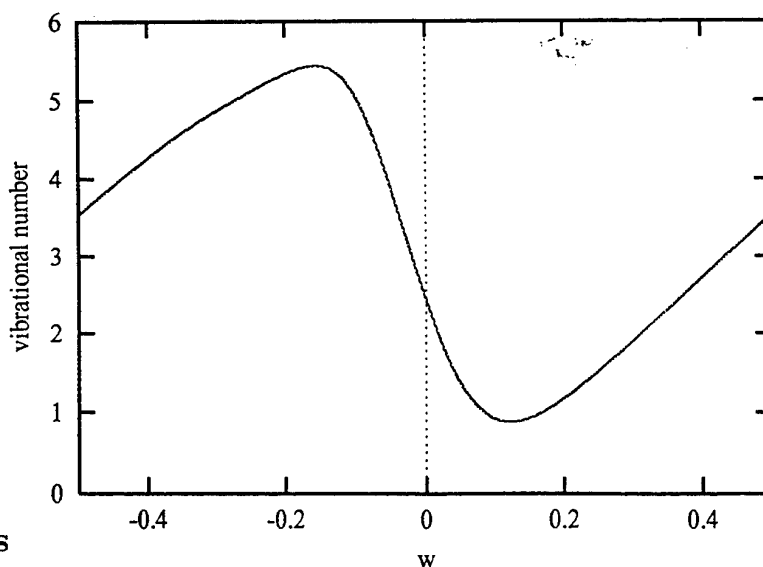
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The theoretical problem of the evaluation of the trajectories of bimolecular three center exchange reactions can be divided into two steps. The first is the construction of the potential energy surface [1,2,3] for the interaction of the reactants while the second is the integration of the equations of motion. In this work we have made use of a new type of hyperspherical non orthogonal bond-order coordinates (HYBO) to integrate the hamilton's equations of motion. These coordinates are defined as  $\rho = \sqrt{n_{AB}^2 + n_{BC}^2}$  and  $\alpha = \arctan(n_{BC}/n_{AB})$  where  $\rho$  is the hyperradius and  $\alpha$  is the hyperangle. In these coordinates the collinear classical hamiltonian reads as

$$H = \frac{1}{2\mu|g|} [F^2 \cot^2 \alpha + (D \tan \alpha - C \cot \alpha)^2 p_\rho^2 + 2 \frac{F^2}{\rho} \cot \alpha - \frac{G}{\rho} (D \tan \alpha - C \cot \alpha) p_\rho p_\alpha + \frac{1}{\rho^2} (F^2 + G^2) p_\alpha^2] + V(\rho, \alpha)$$

where  $\mu$  is the reduced mass of the system, C, D, F and G are constants depending of the value of the equilibrium distances, the reduced masses and the spectroscopic constants of the diatoms. A similar expression can be given for the quantum formulation. The related Hamilton and Schroedinger equations have been solved and product properties have been calculated. An example of the dependence of the product vibrational number from the initial phase of the diatom is given in the figure



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## Time- and Frequency Resolved Photoionisation of Hydrogen-bonded Clusters and Biomolecules: 1-Naphthol(NH<sub>3</sub>)<sub>n</sub> and Adenine

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A combination of time- and frequency-resolved photoionisation permits to investigate the excited-state structure and dynamics of more complicated isolated systems, like hydrogen-bonded clusters or biomolecules.

Excited-state proton transfer (ESPT) in the 1-naphthol(NH<sub>3</sub>)<sub>n</sub> system serves as a model for intracuster reactions. However, until recently there was a debate about the threshold size  $n$  necessary to induce ESPT. While most frequency-domain experiments revealed a threshold size of  $n=4$ , time-domain experiments seemed to indicate  $n=3$ . We carried out time-domain experiments at a variety of pump- and probe wavelengths. If fragmentation in the cluster ion was carefully suppressed, a transient with a time constant of 60 ps appeared in the  $n=4$  channel that was assigned to ESPT.

We also observed the vibrationally resolved UV spectrum of the DNA base adenine. By comparison with the spectrum of 9-methyladenine we demonstrated that the spectrum of isolated adenine is indeed dominated by the N<sub>9</sub>-H tautomere. For the most intense band, presumably the origin, an excited state lifetime of 9 ps was determined. The decay is most likely due to intersystem crossing.

## REMPI-LIF studies of ion-molecule association reactions

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Whilst laser-based techniques have been routinely applied to kinetic measurements in neutral chemistry, they have not been widely used to study ion-molecule reactions. In ion chemistry, kinetic measurements are commonly performed using flow tube techniques coupled with mass spectrometric detection. However, until recently, the use of flow tubes has restricted the range of total pressure over which measurements can be conveniently made and studies of simple ion-molecule association reactions have largely been restricted to kinetics in the low-pressure limit. Here we report the use of a laser technique based upon Resonance Enhanced Multiphoton Ionisation (REMPI) for ion production and laser-induced fluorescence (LIF) for ion detection which allows us to extend significantly the range of pressures over which ion-molecule association reaction kinetics can be studied.

Our work focuses on the pressure-dependent kinetics of the archetypal ion-molecule association reaction:



This reaction is of key importance in a number of high pressure plasma environments. For example, in the terrestrial atmosphere, the  $\text{N}_2^+$  radical cation is readily produced by ionising radiation or electrical phenomena. At altitudes where pressures are significant ( $>1$  Torr), Reaction [1] is a major route to removal of  $\text{N}_2^+$  ions.

In this work, we study Reaction [1] under conditions of 1-13 Torr for  $\text{M}=\text{N}_2$  and 10-950 Torr for  $\text{M}=\text{He}$ . In both pressure ranges, the kinetics of the reaction are found to deviate significantly from the low-pressure limiting kinetics. Indeed for reaction in He, a significant portion of the fall-off range is covered. Detailed information on both the bond energy<sup>1</sup> and structure<sup>2</sup> of the  $\text{N}_4^+$  ion is available which allows us to apply statistical theories to this particular reaction. A discussion of the results of these calculations in reproducing both the fall-off behaviour observed here and the temperature-dependence of the low pressure limiting rate constant<sup>3</sup> will be presented.

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## Laser Excitation Spectroscopy of Aluminum Containing Free Radicals

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We have measured the laser induced fluorescence ( LIF ) spectra of the aluminum containing free radicals, AlOH and AlNC/AlCN, under the supersonic free jet expansion condition. The radicals were produced in supersonic free jet expansions by reacting the corresponding fragments produced in an Ar plasma with Al atoms evaporated using laser ablation of the metal surface. The spectral search of AlOH was guided by the results from the *ab initio* calculations. The *ab initio* results predict a linear geometry of the  $\tilde{X}^1\Sigma^+$  state of AlOH, while a bent structure of the  $\tilde{A}^1A''$  state. According to the *ab initio* prediction, the electronic transition of AlOH was observed at the near UV region, and the LIF excitation spectrum and the LIF dispersed spectra from the single vibronic levels were measured. On the basis of the rotational and vibrational structures obtained from the spectral analysis, the molecular structures and dynamics will be discussed.

## FEMTOSECOND OBSERVATION OF A $2\sigma / 1\sigma^*$ BOND MAKING IN A SULFUR-CENTERED RADICAL ANION

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Detailed investigations of primary events involved in the formation of a sulfur-centered radical anion ( $\text{CH}_3\text{S} \cdot \cdot \text{SCH}_3^-$ ) have been performed by femtosecond UV absorption spectroscopy at 294K. Following a two-photon electron delocalization in neat liquid dimethylsulfide (DMS), a odd electron bonded intermediate  $(\text{CH}_3)_2\text{S} \cdot \cdot \text{e}^- \cdot \cdot \text{S}(\text{CH}_3)_2$  populated in less than 350 fs has been detected. The real-time probing of an electron trapped by fluctuating configurations of liquid DMS raises the existence of a continuous spectral shifting that parallels the formation of a sulfur-centered radical anion ( $\text{CH}_3\text{S} \cdot \cdot \text{SCH}_3^-$ ). In the temporal range 300 - 1600 fs, the observed red shift ( $\sim 21 \text{ meV}/100 \text{ fs}$ ) is interpreted as an indicator of the electronic-structure reorganization of the transient  $(\text{CH}_3)_2\text{S} \cdot \cdot \text{e}^- \cdot \cdot \text{S}(\text{CH}_3)_2$  complex toward a nascent  $\sigma$  sulfur-sulfur radical anion ( $\text{CH}_3\text{S} \cdot \cdot \text{SCH}_3^-$ ). We suggest a correlation between the early spectral red shifting and a decrease of the splitting magnitude between an orbital characterized by a strong  $\sigma$  lone pair and a  $\sigma^*$  orbital having a « p » lone pair ( $2\sigma$ - $1\sigma^*$  transition). These time dependent spectral data raise the role of favorable angular orientation of the interacting p orbitals for an efficient orbital overlap during the  $2c$ ,  $3e$  S  $\cdot \cdot$  S bond making.

The ultrafast absorption spectroscopy of a nascent  $\text{CH}_3\text{S} \cdot \cdot \text{SCH}_3^-$  radical provides some experimental basis on which MD simulations may be used to explore the stretching of the internuclear S-S distance of a parent  $\sigma$  bond on antibonding electron addition.

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## FTMW Spectroscopy and Determination of the Rare gas–OH, and –SH Complexes

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Rare gas–OH and rare gas–SH complexes are interesting species to understand intermolecular interactions between an open-shell species and a closed-shell species, where these open-shell species have prominent fine and hyperfine structures, and various complicated interactions can exist when they form a complex with other species undergoing large amplitude internal motions. So far, a number of investigations have been performed for complexes of OH and SH with various rare gases. In a recent paper, we have reported a successful analysis of the large amplitude internal motions of Ar–SH studied by FTMW spectroscopy, where we have developed a program system explicitly treating the large amplitude stretching and bending motions which are coupled by fine and hyperfine interactions, where results of relatively large scale *ab initio* calculations were used for the initial parameters for the inter-molecular potential functions.<sup>1</sup>

In order to check the validity of the analysis for Ar–SH, and obtain systematic data for related complexes, we have started studies of Ne–SH and Kr–SH by using FTMW spectroscopy by referring the data obtained by LIF spectroscopy.<sup>2</sup> At present, we were able to observe several pure rotational transitions for both of the species, where spectral pattern of the Kr containing species are relatively regular, while that of Ne species seems to be more irregular. Detailed analysis of the observed spectra are now in progress to extract intermolecular potential functions.

Compared to the SH complexes, where experimental data are rather limited, OH complexes have been studied more extensively, especially for Ar–OH, where a number of excited states of vdW motions have been observed by SEP spectroscopy.<sup>3</sup> We have combined our FTMW data with the SEP data for the analysis, and were able to determine rather accurate intermolecular potential function by using the same program system, confirming the validity of the analysis applied for Ar–SH. Analyses of other rare gas complexes, Ne–OH and Kr–OH are also in progress, where we have observed their pure rotational spectra by FTMW spectroscopy.

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**Formation of vibrationally hot ethynyl radical from the VUV photolysis of acetylene;  
application to astrochemistry**

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Photodissociation mechanisms of acetylene have been studied via fragment fluorescence detection following resonant excitation of the molecular Rydberg states converging to the first IP. Indeed acetylene Rydberg states are the only excited electronic states which carry reasonable absorption oscillator strength in the spectral region 8-11.4 eV (IP), where the interstellar radiation flux is still important to induce molecular fragmentation and radical formation. On the other hand these states are more or less predissociated and can be considered as doorways towards molecular dissociation.

Carbonated fragments, as C<sub>2</sub>H, CH and C<sub>2</sub> were searched by VUV excitation of C<sub>2</sub>H<sub>2</sub> in experimental conditions very similar to those of circumstellar envelopes. Thanks to the remarkable spectral resolution of the new synchrotron beam line SU5 at Super-ACO (12 mÅ in the range 248-65 nm), *rotationally resolved* spectra of Rydberg states of acetylene could be observed through their photofragment visible fluorescence. The dispersed fluorescence from the excited fragments arising from the VUV photodissociation of acetylene was collected by an original sensitive fluorescence detection device, including an ellipsoidal mirror coupled through an optical fiber bundle with a Jobin Yvon 270M monochromator equipped with a sensitive CCD matrix detector.

Below IP, the only observed fragment is C<sub>2</sub>H in its excited A <sup>2</sup>Π state with large vibrational excitation, especially in the bending mode. The observation of a visible continuum emission from this ethynyl radical was performed with increasing Rydberg excitation. The formation of a very hot fragment in the bending mode involving high vibrational levels on top of the barrier of isomerisation has been *theoretically* explained by an increasing amount of excess energy in this bending mode as the mother molecule predissociates in a rather slow time scale as compared to the nuclear motion.

In addition to dehydrogenation, another important relaxation process is suspected in the VUV photolysis of acetylene, isomerisation into vinylidene radical, although there is no direct experimental evidence for it. In order to characterise better this very important and reactive radical, ab initio calculations of the vinylidene radical have been undertaken up to the region of 10 eV. Stable excited singlet states of this radical have been found as well as transition states towards the excited electronic states of linear acetylene. These calculations should stimulate new spectroscopic experiments in order to better characterise this very important and reactive radical.

**The Vinyl Radical ( $\tilde{A}^2A'' \leftarrow X^2A'$ ) Spectrum Between 530 and 415 nm:  
Vibrational and rotational spectra of  $C_2H_3$  and  $C_2D_3$**

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Cavity ringdown spectroscopy has been used to measure the  $\tilde{A}^2A'' \leftarrow \tilde{X}^2A'$  spectrum for vinyl ( $C_2H_3$ ) and deuterated vinyl ( $C_2D_3$ ) between 530 and 360 nm. The first four vibrational features of the vinyl radical  $\tilde{A}^2A'' \leftarrow \tilde{X}^2A'$  spectrum have been analyzed. They correspond to excitation to the  $\tilde{A}^2A''$  state vibrationless level and to three separate vibrational levels with one quanta of excitation in  $\nu_1$ ,  $\nu_4$  and  $\nu_5$  respectively. Rotational contours of these bands have been fit, allowing estimation of the bond angle that the  $\alpha$ -hydrogen makes with the C-C bond axis. Average values of these angles that are obtained for each of the  $\tilde{A}^2A''$  levels fit are consistent with the assignment of these bands to the particular normal modes. The predissociation lifetime is about 4 ps in the first two vibrational levels of the  $\tilde{A}^2A''$  state, and decrease abruptly to less than 2 ps for levels 1200  $cm^{-1}$  above the vibrationless level in excited electronic state. The band contours also change above 1200  $cm^{-1}$  and could not be fit assuming the molecule was a planar asymmetric top.

Table I. Best fit for vinyl radicals ( $C_2H_3$ ) using the AsyTopBand program

Wavenumber	19700 ~ 20150	20750 ~ 21150	21010	~ 21400
Vibrational	$0_0^0$	$1_0^1$	$5_0^1$	$4_0^1$
Band origins	20029(1)	20967(1)	21213(1)	21285(1)
Rotational constants				
A	6.310(3)	6.574(2)	6.456(4)	6.530(5)
B	0.981(1)	0.963(1)	0.970(1)	0.966(0)
C	0.848(1)	0.840(0)	0.844(0)	0.842(1)
Angles ( $\angle C_2C_1H_1$ )	108.9(1)	115.75(15)	112.9(1)	114.7(5)
Bandwidths	1.2(3)	1.2(3)	2.8(3)	2.8(3)
Bond lengths in Å, bond angles in degrees, band origin and rotational constants in $cm^{-1}$				

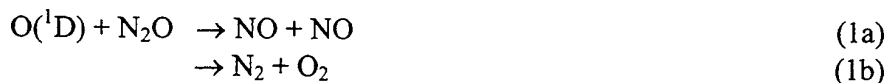
# Time resolved FTIR emission in the $O(^1D) + N_2O$ reaction

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Time resolved infrared emission has been observed resulting from the photolysis of various oxides of nitrogen, and here we concentrate on the emission following the 193 nm photolysis of  $N_2O$ . Emission was observed with a FTIR spectrometer operating in step scan mode, and this allows observation of all the emitting states as a function of time, with the wavelength range and time resolution dependent only on the properties of the IR detector. Nascent product distributions can be found, rates of relaxation determined, and under conditions where energy is transferred from one species to another, the kinetic behaviour of both donor and acceptor can be determined.

At 193 nm the photolysis of  $N_2O$  produces  $O(^1D)$ , and the subsequent reaction



has a branching ratio of  $k_{1a}/(k_{1a}+k_{1b})$  of approximately 0.5. Strong emission from NO is seen, and the nascent vibrational distribution can be obtained from the time resolved emission spectrum in the presence of Ar to ensure rotational thermalisation. Of particular interest is the first overtone emission,  $\Delta v = -2$ , near  $3600\text{ cm}^{-1}$ , where the spectral structure allows the vibrational distribution to be easily obtained because of a fortuitous constructive interference of the individual emission bands. Spectra in both the overtone and fundamental regions will be shown, and yield the same vibrational distribution. Results in the literature show considerable discrepancies. A potential reason for this is that previous work has used techniques involving the uv excitation of the NO (A-X) transition, and extraction of vibrational populations needs clear knowledge of the relevant excitation and sometimes emission probabilities over wide wavelength ranges. Here we need only Einstein A factors to extract the data: the price is one of sensitivity, but as will be shown nascent distributions can be found for transitions with A factors as low as  $1\text{ s}^{-1}$ . Rotational excitation in the NO product has been observed in emission measurements taken at low pressures. Emission from  $N_2O$  is also seen, but it remains unaffected in the presence of Xe, a good quencher for  $O(^1D)$ , whilst the emission from NO is drastically reduced. We conclude that the energy transfer process to  $N_2O$  from  $NO(v)$  is not as efficient as that from the nascent  $N_2$  produced in the photolysis of  $N_2O$ .

Further studies on the 248 nm photolysis of  $NO_2/N_2O_4$  have yielded emission from overtone and fundamental bands of both NO and  $NO_2$ , with the former produced in photolysis of  $NO_2$ , and the latter by both photolysis of  $N_2O_4$  and by energy transfer. Elucidation of nascent distributions and vibrational state dependent energy transfer rate constants will be described.

**Superhyperfine Interactions in the Open-shell Complex NO-HF:  
Evidence for Electron Transfer in Weakly Bound Complexes**

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High resolution microwave fourier transform spectroscopy has been performed on the open-shell complex NO-HF. The rotational fine structure is largely that expected from the infrared spectrum. However associated with each rotational transition there is a rich hyperfine structure, each transition possessing approximately 40 hyperfine components. These are shown to be due to the magnetic interaction with the hydrogen and fluorine nuclei in addition to that expected for the nitrogen nucleus. In order to interpret the superhyperfine structure from the H and F nuclei, a new hyperfine Hamiltonian has to be derived as the conventional Frosch and Foley theory for linear radicals is inappropriate in these circumstances. An alternative treatment has been developed for intermolecular hyperfine interactions based on a dipolar model for both electron spin and orbital magnetic moments. These results of this will be summarised.

Analysis of both the fine and hyperfine structure indicates a bent geometry with the a-axis NO angle of about  $44^\circ$ . An intermolecular distance of  $3.44 \text{ \AA}$  can also be determined. The fine structure is sensitive to the strength of the Renner Interaction which tends to quench the orbital angular momentum of the NO but is insensitive to its sign. However the hyperfine structure uniquely shows that the unpaired  $\pi^*$  has a lower energy in the plane of the complex.

The measured Fermi contact interaction of the H and F nuclei show that there is unpaired electron density on the HF molecule. The constants have opposite signs and comparison with *ab initio* calculations suggest assigning the larger positive value to the F nucleus. Mechanisms for the transfer of unpaired electron density to the HF molecule will be presented.. Throughout high quality *ab initio* calculations have been used to help interpret the nature of the intermolecular potential energy surface and to understand the nature of the Renner interaction.

## The Electronic Spectroscopy of The C<sub>3</sub>Ar/Kr Complexes

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The  $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma_g^+$  system of C<sub>3</sub> has been used to study the C<sub>3</sub>Ar and C<sub>3</sub>Kr complexes by both laser-induced fluorescence ( $\Delta\nu \approx 0.2 \text{ cm}^{-1}$ ) and wavelength resolved emission ( $\Delta\nu \geq 9 \text{ cm}^{-1}$ ) techniques. From the analyses of the emission spectra, guided by our ab initio calculations, deeper van der Waals potential wells were observed in the bending excited states ( $\nu_2=4-7$ ) of C<sub>3</sub>( $\tilde{X}$ ), especially in the in-plane bending excitation. Since the bending frequency of C<sub>3</sub>( $\tilde{X}$ ) is very low, it is extremely sensitive to probe the dependence of the van der Waals force on the vibrational excitation of the monomer. The Renner-Teller splitting of the C<sub>3</sub>Kr can be estimated as  $4 \text{ cm}^{-1}$  when the C<sub>3</sub> monomer is at the K=1 sublevel of the  $\tilde{A}(0,2^-,0)$  level; but that of the C<sub>3</sub>Ar complex can not be determined with our present resolution. Higher resolution work is in progress.

## High-Resolution Infrared Spectroscopic Determination of the $\nu_5^{\pm n}$

### Vibrational Energies of HCCN and DCCN

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#### ABSTRACT

The high-resolution infrared kinetic spectra of HCCN and DCCN have been recorded, the former between 3395 and 3481  $\text{cm}^{-1}$  and the latter in the 2516-2587  $\text{cm}^{-1}$  region. A total of four dominant Q branches were observed and have been subsequently assigned to the  $\nu_1+2\nu_5^{\pm 2} \leftarrow \nu_5^{\pm 1}$ ,  $\nu_1+3\nu_5^{\pm 3} \leftarrow 2\nu_5^{\pm 2}$  bands of the two isotopomers. The band origins have been determined to be 3420.6675(6), 2544.7427(9), 3460.9116(8) and 2573.4795(7)  $\text{cm}^{-1}$  respectively. In addition a weak series of lines has been tentatively attributed to the  $\nu_1+3\nu_5^{\pm 3} \leftarrow 3\nu_5^{\pm 3}$  hot band of HCCN and the band origin has been determined to be 3188.0463(9)  $\text{cm}^{-1}$ .

These new values have been used in conjunction with the previously published  $\nu_1+2\nu_5^{\pm 2} \leftarrow 2\nu_5^{\pm 2}$  band origins of HCCN and DCCN to obtain  $2\nu_5^{\pm 2} \leftarrow \nu_5^{\pm 1}$  vibrational energies of 212.821(6) and 133.106(5)  $\text{cm}^{-1}$  for HCCN and DCCN respectively. The  $3\nu_5^{\pm 3} \leftarrow 2\nu_5^{\pm 2}$  energy gap of HCCN was also determined as 272.864(5)  $\text{cm}^{-1}$ . Finally, Semi-rigid Bender calculations of the energy levels of these molecules have been carried out showing reasonable agreement with experimental data though some apparent discrepancies remain unexplained.

**Atomic excited-state magnetizabilities from Doppler-free two-photon absorption measurements in high magnetic fields**

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The complete atomic Zeeman hamiltonian contains the term  $-\frac{1}{2}\hat{\xi}_{zz}B^2$  where  $B$  is the magnetic field in the  $z$  direction and  $\hat{\xi}_{zz}$  is the magnetizability operator. It bears valuable information about the electronic structure but is small and causes only weak field induced second-order energy and frequency shifts. Normally these are masked by the strong first-order Zeeman effects of the permanent electronic orbital and spin magnetic moments. We have utilized the Doppler-free two-photon absorption technique in a cryomagnet with suitable selection rules in order to extract the magnetizability term for atoms in excited states. The transitions started from the ground states of the stable alkalines (Li, Na, K, Rb, Cs) and of the earth alkalines Ca, Sr, and Ba. Special cells had to be constructed allowing for vaporization at temperatures up to 1000 degrees Celsius close to the superconducting coils of the magnet. The experimental results of the one-electron systems can be understood in terms of a constant-core hydrogen model while those of the two-electron systems are harder to analyze because of the presence of strong spin-orbit interactions. Ab-initio computations were carried out for comparison but convergence could not be achieved for some of the heavier atoms.



**Perturbation-facilitated optical-optical double resonance spectroscopy of  
the  $1_u(^1D)$  and  $2_u(^1D)$  ion-pair states of  $I_2$   
through the parity mixing intermediate state**

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This paper is a part of the series of works to elucidate the energy levels of the ion-pair states of  $I_2$  by optical-optical double resonance. This technique is unique in combining the  $X^1\Sigma_g^+$  ground state with the ion-pair state in the two-step excitation through the intermediate state. We have accessed *gerade* states in the  $(1 + 1)$  photo-excitation process and *ungerade* states in the  $(1 + 2)$  process in view of the parity selection rules for the optical transitions:  $g - u$  for an one-photo transition, and  $g - g$  or  $u - u$  for a two-photon transition. Either the  $A^3\Pi(1_u)$  or  $B^3\Pi(0_u^+)$  valence state was usually used as an intermediate in terms of the  $\Omega = 0$  propensity rule for the valence to ion-pair state transitions having the charge transfer property along the internuclear axis.

In the present paper, we demonstrate the extension of this technique, an essentially perturbation-facilitated optical-optical double resonance spectroscopy, to the study of the  $1_u(^1D)$  and  $2_u(^1D)$  states correlating with  $I(^1S) + I(^1D)$  at the dissociation limit. The  $B^3\Pi(0_u^+) \sim c1_g$  parity mixing state is used as an intermediate to excite the molecules in the  $(1 + 1)$  photon-excitation scheme. This technique has an advantage that we are able to probe the ion-pair states of *ungerade* symmetry in the one-photon transition from the intermediate state instead of the much weaker coherent two-photon transition used before. Furthermore, the  $c1_g$  state has the strong Franck-Condon overlap with the ion-pair states and permits to access a wide range of the vibrational levels. Even though the  $g-u$  coupling by the hyperfine interaction allows to mix the different  $J$  levels, the second step of the double resonance is analyzed on the basis of the  $B^3\Pi(0_u^+)$  and  $c1_g$  coupling scheme elucidated in the transitions to the known  $F0_u^+(^3P_0)$  and  $H1_u(^3P_1)$  states. We can detect the transitions to the  $1_u(^1D)$  state in the  $0 \leq v \leq 31$  and  $9 \leq J \leq 103$  ranges, and also the transitions to the  $2_u(^1D)$  states in the  $0 \leq v \leq 9$  range. The  $1_u(^1D)$  and  $2_u(^1D)$  states are analyzed with including their heterogeneous coupling and their molecular constants are derived.

THE INFRARED SPECTRA OF IONS DERIVED FROM ALLENE AND PROPYNE  
AND TRAPPED IN SOLID NEON

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When a Ne:allene or a Ne:propyne sample was codeposited at approximately 5 K with a sample of pure neon that had been excited in a microwave discharge to provide a 16.6-16.85 eV energy source, prominent new infrared absorptions which can be assigned to the allene and propyne cations and to the allenyl anion resulted. Comparison of the product spectra observed in experiments on the various isotopically substituted precursor molecules with the vibrational fundamental patterns obtained from density functional and *ab initio* calculations is crucial to the positive identification of these three products. These results may be contrasted with those of the corresponding gas-phase studies, in which *cyc*-C<sub>3</sub>H<sub>3</sub><sup>+</sup> predominates in this excitation energy range. In the present experiments, collisions with the excess of neon atoms in the sampling region rapidly remove excess energy from the initially formed allene and propyne cations, inhibiting the loss of an H atom from those two species.

THE INFRARED SPECTRUM OF THE  $\text{NH}_4^+$  CATION TRAPPED IN SOLID NEON

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Both of the infrared-active vibrational fundamentals of the  $\text{NH}_4^+$  cation trapped in solid neon have been observed near the corresponding gas-phase band centers. Experimental conditions favoring the stabilization of this species--the first protonated molecule to be prepared in a neon matrix environment--will be explored. The study was extended to the partially and fully deuterated ammonium cations, for which the first infrared spectroscopic data will be reported.

Isotope  $^{18}\text{O}/^{16}\text{O}$  ratio measurement of water vapor using cavity ringdown spectroscopy

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We applied a cavity ringdown spectroscopy technique, which is one of the most promising methods for quantitative trace-gas measurement, to the direct laboratory measurement of the  $^{16}\text{O}/^{18}\text{O}$  isotopic ratio in water vapor.

The rovibrational transitions of water near 950 nm was utilized for a quantitative absorption measurement of water molecules. The Nd:YAG laser-pumped dye laser system was operated as a tunable light source, producing 3mJ/pulse (repetition rate of 10 Hz) in the region of 920-960 nm. The line width was estimated to be  $0.04\text{ cm}^{-1}$  and the duration of the laser pulses 7 ns (FWHM). The laser radiation that passes through the ringdown cavity is focused onto a InGaAs photodiode, with the transient signal being recorded by a digital oscilloscope. Typically 28 waveforms were averaged, then the sum transferred to a computer and fit to a single exponential decay. The decay constant was converted to the total loss per pass and saved as a point in the spectrum.

We first examined the pressure dependence of line width in the CRD spectra by changing the pressure of the buffer gas  $\text{N}_2$ . The optimum condition for the quantitative measurement was found to be the water partial pressure of 5 torr and the total pressure of 250 torr. We could consequently confirm that the peak intensity of the CRD spectra in the 950 nm region is proportional to the line strength in the HITRAN database. Two water samples, VSMOW and SLAP, were used to the feasibility of the system developed for the isotope ratio measurement. For each sample, we have observed the CRD spectra of the  $\text{H}_2^{18}\text{O}$  and  $\text{H}_2^{16}\text{O}$  and calculated the peak intensity of spectral line by fitting the spectra with Voigt profile function. The value obtained for the difference between two samples is  $\delta^{18}\text{O} = -55 \pm 7\%$ , which is an improvement over that measured with the photoacoustic spectroscopy.

## Triplet Acetylene in the Vibronic Excited State

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Acetylene in the lowest triplet state ( $T_1$ ) has three local minima at *cis*, *trans*, and *vinylidene* configurations according to theoretical calculations. Isomerization reaction among those configurations has been paid a lot of attentions. We have observed an electronic transition between the  $T_2$  -  $T_1$  potential surface at the *cis*-bent configuration around  $7400\text{ cm}^{-1}$  region by using near-IR diode laser kinetic spectroscopy combined with a pulsed mercury photo-sensitized reaction. By now 0-0 band of  $C_2H_2$ ,  $C_2HD$  and  $C_2D_2$  have been rotationally analyzed and sever inhomogeneous rotational perturbations have been recognized in some specific  $K_a$  states in the lowest triplet state of  $C_2H_2$ , but no perturbations were observed in  $C_2HD$  and  $C_2D_2$ . The perturber for the  $K_a=1$  state of vibrational ground state in the lowest triplet state is a mystery. One candidate for this perturbation is an interaction among the other isomers. Some high level *ab initio* calculations predicted that there is a potential minimum at the *trans*-isomer configuration with a small potential barrier in both the  $T_2$  and  $T_1$  surfaces. In case of  $T_2$ , the *trans* minimum is predicted to be lower than the *cis*. Therefore, an interaction between the *cis* and *trans* should be expected, especially when some vibrational modes are excited. Recently we have observed 1-0 band of  $C_2H_2$  and  $C_2D_2$  in  $8170$  and  $7970\text{ cm}^{-1}$  region, respectively, in which the *cis*-bent vibrational mode is excited. After the rotational analysis based on the combination difference, more sever perturbations have been recognized. Moreover, the rotational constant around the C=C axis is abnormally enlarged by the vibrational excitation. This strong Coriolis type interaction may suggest a possibility of the isomerization reaction because the rotational quantum number of  $K_a$ , which is the angular momentum along the C=C axis, can be a motion of constant in the isomerization including the linear configuration. In order to discuss such an interaction between different point groups as *cis* ( $C_{2v}$ ) and *trans* ( $C_{2h}$ ) configurations, Complete Permutation Inversion group  $G_8$  should be introduced as a common symmetrical platform.

## Intracuster hydrogen atom transfer reactions of benzophenone in the photoexcited and photoionized states

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Two-photon ionization of aromatic solvent (Sol) moiety and intracuster ion-molecule reactions in benzophenone(BP)/Sol binary clusters have been studied by using laser induced fluorescence and resonance enhanced multiphoton ionization (REMPI) time-of-flight (TOF) mass spectroscopic methods. Sol molecules examined are benzene (Bz), fluorobenzene (f-Bz), toluene (Tol), 1,4-dimethoxybenzene (DMB) and N,N-dimethylaniline (DMA). All the TOF mass spectra were dominated by  $(\text{Sol})_n^+$  signals.

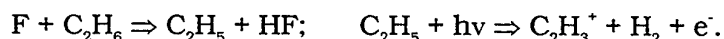
In the clusters with Bz and f-Bz, intracuster electron transfer from BP to  $\text{Sol}^+$  was observed to occur after two-photon ionization of the Sol moiety. In the clusters with DMB and DMA, the ionization yields of the Sol part were extremely low, which may be due to charge transfer induced efficient electronic quenching of the  $S_1$  state of the Sol part. In the clusters with Tol,  $\text{BP}^+$ ,  $[\text{BPH}]^+$  and  $[(\text{BP})_2\text{H}]^+$  appear in the REMPI mass spectrum, but no  $[(\text{BP})_m(\text{Tol})_n]^+$  signals ( $m, n \geq 1$ ) were observed. Within  $[(\text{BP})_m(\text{Tol})_n]^+$  clusters, Tol<sup>+</sup> moiety undergoes electron transfer reaction with BP to yield  $\text{BP}^+$ . Dominant intracuster reactions to produce  $[\text{BPH}]^+$  or  $[(\text{BP})_2\text{H}]^+$  are hydrogen atom transfer reactions of  $\text{BP}^+$  or  $(\text{BP})_2^+$  with surrounding Tol and proton transfer from  $\text{Tol}^+$  to BP or  $\text{BP}_2$ . There is a possibility that the photoionization of  $(\text{Tol})_2$  yields  $\text{Tol}^+(\text{Tol})$  which undergoes dissociation yielding hydrogen atom and benzyl cation. The mass number of the product of this process,  $\text{C}_7\text{H}_7^+(\text{Tol})$  is 183 which is the same as that of  $\text{BPH}^+$ . Intracuster ion-molecule reaction of deuterated toluene ( $\text{CD}_3\text{C}_6\text{H}_5$ ) was also investigated in order to assign the specie of mass number 183. In a BP/  $\text{CD}_3\text{C}_6\text{H}_5$  binary system, mass number of 184 dominantly appeared instead of 183, which strongly suggests that the specie with mass number 183 is  $\text{BPH}^+$  in BP/Tol binary clusters. According to the results together with ab initio calculation of protonated BP's, the structure and the stability of  $[\text{BPH}]^+$  and  $[(\text{BP})_2\text{H}]^+$  will be discussed in detail.

Besides the intracuster ion-molecule reactions, intracuster photoreaction of BP in BP/1,4-cyclohexadiene binary clusters was also investigated by means of a laser induced fluorescence method. Strong fluorescence of BP ketyl radical was observed in relatively large clusters, while exciplex emission was dominantly seen in relatively small clusters. Possible explanation for this size dependent intracuster reaction of photoexcited BP will be proposed.

## Photoionization Mass Spectrometric Study of the Dissociative Ionization of Ethyl Radical: Heat of Formation of Vinyl Radical

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The C-H bond dissociation energy of ethylene and the corresponding heat of formation of the vinyl radical,  $C_2H_3$ , were hotly contested for many years [1-4]. The main discrepancies were between the so-called «kinetic» studies and «ion» or spectroscopic studies. Although the difference of around 5 kcal/mol might seem to have been resolved in two recent papers that are based on kinetic measurements [3-4], the general issues appear to remain [5]. In the present work, the heat of formation of  $C_2H_3$  was determined *via* the appearance energy technique. In this method, vinyl cations were produced from the dissociative ionization of ethyl radicals that were, in turn, generated in a flow tube reactor via reaction of F-atoms with ethane, as in the following sequence:



In this study, the discharge flow-photoionization mass spectrometer apparatus, which is operated on beamline U11 at the National Synchrotron Light Source [6], was employed to determine the threshold for  $C_2H_3^+$  formation from  $C_2H_5$  radicals. The result obtained for  $\Delta H_f(C_2H_3)$  in the present study, about  $72 \pm 2$  kcal/mol, is in excellent agreement with those of other spectroscopic studies [2] and with the two most recent kinetic studies [3-4]. It is therefore another piece of evidence in favor of the «higher» heat of formation of  $C_2H_3$  and it refutes the older kinetic studies.

### Acknowledgments:

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## Photoionization Mass Spectrometric Study of t-Butyl Radical: Ionization Energy and Heat of Formation

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In this study, a discharge flow-photoionization mass spectrometer apparatus, which is operated on beamline U11 at the National Synchrotron Light Source [1], was employed to determine the threshold for t-butyl ion formation from t-butyl radicals. Tertiary-butyl radicals were generated in a flow tube *via* reaction of F-atoms with either iso-butane or t-butyl iodide. Photoionization efficiency (PIE) spectra for ions formed in this way were indistinguishable. The ionization energy was determined from the ionization threshold by two methods. As a first cut, the rise of ion signal above the background level was evaluated. A more precise determination was made by differentiating the PIE curve to obtain a plot that looks much like a photoelectron spectrum. The ionization energy for t-butyl radicals was thus determined to be  $6.82 \pm 0.02$  eV.

Additional experiments were performed to measure the threshold for t-butyl ions formed via dissociative ionization of t-butyl iodide. In this way, it was possible to derive the heat of formation of t-butyl radicals. Taking this  $\Delta H_f$  result, along with standard thermodynamic values, the absolute proton affinity for iso-butane was readily determined. All the results of the present study are compared with those of previous experimental and theoretical investigations.

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## Spectroscopy of radicals in superfluid liquid Helium droplets

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We have coupled a pyrolysis source to a helium droplet apparatus in an effort to obtain free radical IR spectra. Initial results of this apparatus are reported. Infrared spectra in superfluid liquid helium droplets have been obtained for hydrogen peroxide, as well as clusters of halogens and hydrogen peroxide with HCN. Upon heating the pyrolysis source, the infrared absorption bands of the pyrolysis products and their associated clusters with HCN at different source-temperatures up to 1400 K are observed.

Initial surveys are taken within strong electric fields to measure the pendular state vibrational frequencies of the species formed. Successively taken field-free spectra allow the determination of the molecular structures of the clusters.

QUENCHING OF VIBRATIONALLY EXCITED  
Na<sub>2</sub> MOLECULES IN COLLISION WITH Na ATOMS  
AT ULTRACOLD TEMPERATURES

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There is a growing number of experiments aimed at producing large quantities of cold and ultracold molecules in traps. The major problem in forming a molecular Bose-Einstein condensate is the instability due to collisional processes. Little is however known about molecular inelastic and reactive collisions at the ultralow translational energies encountered in traps [1, 2, 3].

Accurate studies of molecular collisions at thermal energies are now performed in several laboratories with sophisticated theoretical methods but only a few concern the low and ultralow energy range. Using quantum mechanical scattering methods based on hyperspherical democratic coordinates, we have undertaken the study of vibrational relaxation of alkali molecules by collisions with alkali atoms at ultracold temperatures. In this first study, we considered the Na<sub>2</sub> + Na system. We used an ab-initio potential energy surface for quartet symmetry [4]. Inelastic and reactive collisions for total orbital angular momentum  $J = 0$  have been studied. We have obtained cross sections and rate coefficients at ultracold temperatures for total quenching of some ( $v, j = 0$ ) rovibrational states of Na<sub>2</sub>.

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## From Realistic Potential Energy Surfaces to Structure and Dynamics of Atmospheric Dimers.

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New accurate potential energy surfaces for the dimers are available from analysis of molecular beams scattering experiments for our laboratory. In particular, the novel technique developed, first reported in *Nature* in 1994[1], allows the control of the relative orientation of the colliding molecules and so permits observation of a quantum-mechanical interference effect (the "glory"). Analysis of the velocity dependence of the integral cross-section for the scattering showing the glory oscillations provides data which together with accurate second virial coefficient yields the intramolecular potential and thus information on the dimer structure. So it is possible to obtain the anisotropy of the potential energy surfaces, namely the dependence on relative orientation for the dimers  $\text{N}_2\text{-N}_2$ ,  $\text{O}_2\text{-O}_2$  and  $\text{N}_2\text{-O}_2$ . These results indicate that most of the bonding in the dimer comes from electrostatic (van der Waals) forces [2-3].

It is interesting to observe how for these van der Waals complexes, geometry and nature of the dimers differ. We report calculations of the bound rovibrational states of the dimers for  $J \leq 6$  by solving the secular problem over the exact Hamiltonian, considering the monomers as rigid rotors. The full quantum mechanical calculations of bound states are carried out using the program BOUND [4]. We compare our results with other works. Surprisingly we have seen that although the potential energy surfaces can have different topography, they may simulate some spectroscopic observables [5-8], in spite of the fact that geometry and values of well depths and positions differ significantly; what differs is their ability to reproduce all experimental data, particularly integral cross-sections and second virial coefficients, which are therefore crucial for understanding dimer structure.

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## Rate constant measurements and calculations on the reactions of atomic silicon, Si(<sup>3</sup>P), with O<sub>2</sub> and NO at temperatures down to 15 K

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Recent experimental and theoretical studies in the last ten years have shown that reactions between neutral species involving radicals and open-shell atoms can exhibit large rate coefficients ( $k > 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) even at low temperatures ( $T < 300 \text{ K}$ ). Some of these exothermic neutral-neutral reactions recently received more attention in interstellar chemistry because they are supposed to influence profoundly the evolution of molecular abundances in interstellar dense clouds, in which the temperature can be as low as 10 K.

The experimental work has been achieved at the **University of Rennes** using a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) facility associated to the PLP-LIF (Pulsed Laser Photolysis – Laser Induced Fluorescence) technique. Silicon atoms were generated by multiphoton photolysis of Si(CH<sub>3</sub>)<sub>4</sub> using a 266 nm Nd:YAG laser mildly focused, and detected by LIF employing the ( $3p^2 \ ^3P_0 - 4s \ ^3P_1$ ) transition of atomic silicon at 251.43 nm using a MOPO. Both reactions were found to be fast at room temperature and to accelerate when the temperature is lowered. The rate constants temperature dependences obtained experimentally in the range 15 K – 300 K are well fitted by the equations :

$$k(\text{Si}(\text{}^3\text{P}) + \text{O}_2 \rightarrow \text{SiO} + \text{O}) = 1.72 \times 10^{-10} (T/300 \text{ K})^{-0.53} \exp(-17/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k(\text{Si}(\text{}^3\text{P}) + \text{NO} \rightarrow \text{SiN} + \text{O}) = 0.90 \times 10^{-10} (T/300 \text{ K})^{-0.96} \exp(-28/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The relatively large values of the rate constants obtained at low temperatures suggest that adiabatic capture theory is relevant for these reactions. This method, proposed by D. Clary has been successfully applied to neutral-neutral reactions which do not exhibit any activation energy. T. Stoecklin and D. Reignier have undertaken these calculations using this approach at the **University of Bordeaux**. The results of their calculations and comparison with the experimental results will be presented in this poster.

**Cation spectroscopy and molecular properties of the structural isomers of  
methylaniline by mass-analyzed threshold ionization spectroscopy**

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**Abstract**

Mass analyzed threshold ionization (MATI) spectroscopy in conjunction with two-color resonant two-photon excitation was used to investigate the ionic properties of the structural isomers of methylaniline. The adiabatic ionization energies were determined to be  $60160 \pm 5$ ,  $61002 \pm 5$ , and  $61059 \pm 5 \text{ cm}^{-1}$  for *ortho*-, *meta*-, and *para*-methylanilines, respectively. The frequencies of some observed vibrations are found to vary slightly among these structural isomers. The present experimental results are well supported by ab initio and density functional theory calculations.

(as a poster presentation for 26<sup>th</sup> INTERNATIONAL SYMPOSIUM ON FREE  
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**Ionization and Dissociation Mechanisms of Ketene Using  
Resonance-enhanced Multiphoton Ionization Mass Spectrometer: (2+2)  
versus (2+1) Schemes**

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By using a resonance-enhanced multiphoton ionization (REMPI) technique, we have studied ionization and photodissociation mechanisms of ketene. Prior to ionization, the jet-cooled ketene is first excited at a wavelength 355 nm to  $3p_y, 0^{\circ}$  Rydberg state through a two-photon absorption. The (2+2) and (2+1) REMPI schemes may be distinguished depending on the impinging laser energy. If the (2+2) REMPI process dominates, the ketene ion is produced by the autoionization of a superexcited state, which lies in rovibrationally excited Rydberg state. The  $\text{CH}_2^+$  is fragmented following two schemes. One is a consecutive process, i.e., the fragment is produced from the autoionized ketene. This conclusion is supported by a series of measurements of pulse field and pressure effects. The factors of pulse field and collisions may enhance the autoionization rate significantly, imposing the same influence on the ketene ion and  $\text{CH}_2^+$ . The second is a dissociative ionization, i.e., the  $\text{CH}_2^+$  ion is fragmented from the superexcited state in competition with the autoionization. On the other hand, if the (2+1) REMPI scheme dominates under a low ionizing laser energy, the ketene ions are led by a direct photoionization. The increase of either pulse field intensity or interacting duration simply shortens the arrival time of the ketene ion on the detector. Finally, a time-resolved ketene ion spectrum is measured to characterize temporal behaviors for the autoionization and direct photodissociation. The relaxation lifetime for the autoionized ketene is found to be much faster than that for directly photoionized source.

## Collective coordinates for polyatomic reactions and cluster dynamics

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For the general n-body dynamics we have analyzed the properties of configuration space within a symmetric hyperspherical coordinates framework.

These coordinates are conveniently broken up into external (or spatial) rotations, kinematic invariants (related to the inertia moments) and kinematic (internal) rotations [1]. Kinematic and rotational coordinates describe collective and concerted motions respectively.

For a given value of the hyperradius, which is a measure of the total inertia of the system, the space of kinematic invariants is the surface of a right spherical triangle and is described by two angular variables (with proper range) [2].

The dimension of the kinematic space depends on the number of atoms of the system. For tetraatomic systems, this is a three-dimensional surface [3] where we represent particle permutations and internal displacements for which inertia moments are unchanged.

For kinematic invariant space alternative parametrizations are possible. These have been analysed [4] and their usefulness has been shown for the study of constrained intramolecular motions and for the collective motions of polyatomic molecules and clusters. The ammonia umbrella inversion motion (near the oblate top configurations) is a relevant example, but collective motions for other systems, such as hydronium ion and methyl anion can be modelled in kinematic invariant space.

We have shown the structure of the kinematic space for collinear systems [5] (in this case a two-dimensional surface) and we have introduced alternative parametrizations for the study of planar or otherwise constrained systems. Moreover, kinematic coordinates, when used in the mapping of the potential energy surface, easily permit to obtain the correct symmetry with respect to the exchange of the identical particles, especially with reactions which exhibit a collinearly dominated dynamics, such as  $\text{OH} + \text{H}_2$  and  $\text{CN} + \text{H}_2$ .

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## Pressure Dependence of Radical Combination Reactions of $\text{CCl}_3$ at 0.05 to 1000 bar: The Role of Excited Electronic States and Radical Complex Mechanisms

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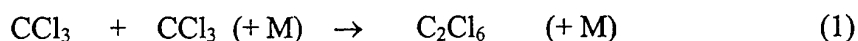
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In thermal radical combination reaction a constant “high pressure” rate constant,  $k_\infty$ , is usually expected, independent of the choice of a bath gas M and up to densities where diffusion control starts to take over. Deviations from standard falloff curves with “turn-ups” from already established “ $k_\infty$ ” at sufficient densities and bath gas dependencies of “high pressure” rate constants will thus provide direct experimental evidence for additional dynamic features of these reactions. Variations in the role of electronically excited product states and the contributions of competing radical-complex mechanisms are most important in this respect – and usually not well understood.

We have studied three related recombination reactions of the  $\text{CCl}_3$  radicals with various reaction partners over a wide pressure range of 0.05-1000 bar at temperatures of 250-350 K, using UV absorption detection technique following 248 nm photolysis of the precursor  $\text{CCl}_3\text{Br}$  for the  $\text{CCl}_3$  radicals in the high pressure flow cell:



These comparative measurements with systematic variations of reaction partners, bath gases ( $\text{M}=\text{N}_2$ , He, Ar, and  $\text{CO}_2$ ) and temperatures show unusual deviations from standard falloff curves with bath gas dependence of supposed high pressure rate constants,  $k_\infty$ , and even pressure dependent upturn of rate constants beyond a pressure range of constant  $k$  before the final onset of diffusion control. A detailed analysis of the data will be discussed with respect to evidence for separated identification of excited electronic state effects and the relative importance of a radical complex mechanism. In addition, the contributions of diffusion controlled kinetics at the highest densities are evaluated as well.



### Fourier Transform Microwave Spectroscopy of TiCl

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In a previous submillimeter-wave pure rotational spectroscopy of TiCl, we obtained accurate rotational constants for four spin components. However, the hyperfine splittings due to the nuclear spin of <sup>35</sup>Cl and <sup>37</sup>Cl had never been detected because of high J involved in the submillimeter-wave lines. For this reason, we investigated lower pure rotational transitions of TiCl in the 24-34GHz region with an FTMW spectrometer combined with a pulsed discharge nozzle. We observed the hyperfine structures of Ti<sup>35</sup>Cl (v=0,1) and Ti<sup>37</sup>Cl (v=0) in the three lowest rotational transitions for the two spin components in the X<sup>4</sup>Φ state near the frequencies predicted with the rotational constants from submillimeter-wave spectra.

TiCl was generated in a supersonic jet by discharging a mixture of TiCl<sub>4</sub> (0.1%) and Ar. The backing pressure was about 3 atm and discharge voltage was 2kV. The lines appeared to be strong, when the color of discharge was radiant blue similar to that for the submillimeter-wave observation.

In the analysis, submillimeter-wave data was also included with appropriate weights. The hyperfine components were fit to the ordinary Hund's case (a)<sub>B</sub> Hamiltonian. Three magnetic hyperfine coupling constants, a, b, c, and an electric quadrupole coupling constant eQq<sub>1</sub> have been determined.



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### **Fluorescence detection of carbon-centered radicals in different systems**

A novel approach employing a pre-fluorescent sensor has been employed to determine the absolute kinetics for end-cleavage in TEMPO-capped polystyrene obtained by 'living' free radical polymerization. This new methodology takes advantage of the suppression of coumarin fluorescence when the chromophore is tethered to a paramagnetic nitroxide. This nitroxide is an excellent free radical trap for carbon centered radicals; upon radical trapping, the resulting diamagnetic alkoxyamine is strongly fluorescent. Thus, fluorescence build-up is a direct measure of free radical formation, and can be employed to quantify their formation, or to study their kinetics. Studies of the temperature dependence of the process can be employed to determine activation parameters and bond dissociation energies. This simple technique can be employed to study the dynamics in the actual polymer systems, overcoming the frequent need to resort to model compounds.

The Coumarin-TEMPO probe has also been used in an aqueous media in order to follow the trapping of free radicals generated in the horseradish peroxidase/hydrogen peroxide system. The probe has shown efficient trapping of the N-acetyl-1-tyrosinamide radical with a consequent increase in the fluorescence signal indicating potentials for the use of this methodology in biological systems.

Actual investigations are concentrated on the use of a Quinoline-TEMPO pre-fluorescent probe (a crystal structure is available) inside an amphiphilic system. This kind of sensor has the potential to monitor photoinduced and thermal radical generation micelles as much as the diffusion of carbon-centered radical through membranes.

## Photodissociation Dynamics of ClOCl in the near UV

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### Abstract

The state-resolved detection of nascent ClO generated from the photodissociation of Cl<sub>2</sub>O parent molecules is performed by observing single color (2+1) laser-induced fluorescence (LIF) and resonance-enhanced multi-photon ionization (REMPI) following excitation in the wavelength range from 337 to 360 nm. The spectra are assigned to the ClO( $C^2\Sigma^-$ ,  $v' = 0 \leftarrow X^2\Pi_{\Omega}$ ,  $v$ ) transitions and their rotational bands are analyzed. The ClO product is observed with an extremely high rotational excitation, but only a moderate vibrational excitation ( $v \leq 3$ ). The rotational population in  $v = 0$  is strongly inverted and peaks around  $J \approx 100$ . The excited electronic state is assigned to a  $^1B_2 \leftarrow ^1A_1$  transition in agreement with recent ab initio calculations, thus removing discrepancies in the assignment of the lowest excited states of Cl<sub>2</sub>O. The mass distribution in the Cl<sub>2</sub>O molecule and the energetics of its UV dissociation are such that the dissociation represents a case where the totally classic impulsive dynamics strongly dominate over quantum mechanical effects resulting from the topology of the involved potential energy surfaces.

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Infrared spectra of OCS-H<sub>2</sub> and OCS-D<sub>2</sub> complexes

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One of the most remarkable developments in molecular spectroscopy is the observation of rotationally resolved spectra of molecules trapped inside ultra-cold helium droplets in molecular beams.<sup>1,2</sup> These results provide a unique microscopic probe of the nature of superfluidity.<sup>3</sup> Recently, similar infrared spectra of weakly-bound complexes in helium droplets have been reported, including OCS-H<sub>2</sub> and -D<sub>2</sub>.<sup>4,5</sup>

We have observed the spectra of isolated OCS-H<sub>2</sub> and -D<sub>2</sub> complexes in the 2062 cm<sup>-1</sup> region of the  $\nu_1$  band of OCS, using a pulsed supersonic slit jet, and a tunable diode laser operating in rapid-scan mode. The laser beam is passed through the jet region 182 times by means of a toroidal mirror system,<sup>6</sup> and the spectrum is calibrated by simultaneously recording spectra of a temperature stabilized etalon and a standard reference gas (OCS). The expansion gas mixtures consisted of about 0.1% OCS and 20% hydrogen in helium carrier, with backing pressures of about 4 atmospheres.

There are no previous published observations of isolated OCS-H<sub>2</sub>. However, Yu and Klemperer<sup>7</sup> have preliminary data on 3 microwave transitions which can be assigned to OCS-*ortho*H<sub>2</sub> on the basis of their hyperfine structure. Our IR spectrum observed using normal H<sub>2</sub> is consistent with these microwave transitions, and is therefore also due to OCS-*ortho*H<sub>2</sub>. The spectrum is that of a near-prolate asymmetric top with *a*-type transitions, but no *b*-type transitions. The band origin, 2062.107 cm<sup>-1</sup> represents a small red shift of -0.094 cm<sup>-1</sup> with respect to the free OCS monomer. Using normal H<sub>2</sub>, there is no evidence for OCS-*para*H<sub>2</sub> transitions, an apparent anomaly which is likely due to OCS-*o*H<sub>2</sub> being significantly more strongly bound than OCS-*p*H<sub>2</sub>. But by using nearly pure *para*H<sub>2</sub> in the expansion gas mix, we can also observe the spectrum of OCS-*para*H<sub>2</sub>, which resembles that of OCS-*ortho*H<sub>2</sub> but with a slightly different origin (2061.997 cm<sup>-1</sup>) and slightly larger rotational constants. Analogous spectra of OCS-*ortho*D<sub>2</sub> and OCS-*para*D<sub>2</sub> have also been obtained, enabling fascinating comparisons with the latest helium droplet data.<sup>8</sup>

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## Free Radical Measurements in Plasma Diagnostics

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Molecular microwave plasmas are used extensively in applications like etching and deposition. The species present in these plasmas are determined by the high degrees of dissociation and the concentrations of chemically reactive radicals within the plasma itself. A detailed understanding of the main plasma processes requires concentration measurements of both stable species and free radicals *in situ*. The inherent characteristics of Tunable Infrared Diode Laser Absorption Spectroscopy (TDLAS) of high molecular selectivity and sensitivity are well suited for measuring stable and transient species concentrations in plasmas. This contribution will give an overview of recent results obtained using TDLAS to study carbon and boron containing free radicals in microwave plasmas. The results contribute to a better understanding of the chemical and kinetic features of these plasmas.

The hypothesis that the methyl radical is one of the most important intermediates in hydrocarbon plasmas used to form carbon films is now well established. The concentration of methyl and 13 other molecules has been measured by TDLAS in microwave plasmas containing methane or methanol precursors [1,2]. Experimental results were complemented by model calculations of the kinetic processes in  $\text{CH}_4\text{-H}_2\text{-O}_2\text{-Ar}$  plasmas. Formation and destruction reactions for all fourteen species were included, and modelled species concentrations tested against TDLAS measurements. In  $\text{B}_2\text{H}_6\text{-H}_2\text{-Ar}$  microwave plasmas TDLAS was used to measure the ground state absorption spectra of BH and  $\text{BH}_3$  [3]. This is the first reported detection of a vibration-rotation spectrum of BH in absorption. At present because line strengths are not known only relative concentrations of BH can be determined by TDLAS. Nevertheless, measurements of relative concentrations of boron bearing fragments gives an insight into the dissociation pathways of diborane in the plasma. Infrared laser measurements have been complemented by optical emission spectroscopy which has been used, primarily, to determine the neutral gas temperature in the plasma via  $\text{H}_2$  and BH emission spectra.

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## Spectroscopy of free radicals in Solid Parahydrogen

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High-resolution spectroscopic techniques have been seldom applied to condensed phase spectroscopy because of the spectral broadening due to strong intermolecular/atomic interactions and inhomogeneity in the condensed phase. However, a marked exception is found for solid parahydrogen; a crystal composed of only  $J=0$  para- $H_2$ . In a series of papers, we have been attempting to utilize solid parahydrogen as a new matrix for high-resolution matrix isolation spectroscopy [1]. We have showed that rotational motion of molecules in solid parahydrogen is almost free as in the gas phase. Moreover, most of the spectral linewidth in the infrared region is sharper than  $0.01\text{ cm}^{-1}$  at low temperatures. The spectral resolution of  $0.01\text{ cm}^{-1}$  is high enough to discuss intermolecular interactions and molecular motions in the condensed phase in great detail.

Here we focus on free radicals produced by photolysis in solid parahydrogen. As is discussed repeatedly by a number of previous workers, matrix isolation spectroscopy using conventional rare gas matrices often fails to trap in-situ photodissociation products on account of the unfavorable cage effect. However, owing to the very weak intermolecular interaction and the large intermolecular distance as well as the large zero-point lattice vibration, solid parahydrogen becomes a very soft medium for guest molecules. As a result, the photoproducts can be separated in the solid far enough to be stabilized. For example, the UV photolysis of methyl iodide isolated in solid parahydrogen yields methyl radicals very efficiently. The stabilized reactive molecules are subjected to detailed studies on structure and rovibrational motion as well as quantum tunneling chemical reaction with a surrounding hydrogen molecule by high-resolution infrared spectroscopy. Especially, it should be noted that all the fundamental vibrational frequencies of the radicals can be easily identified since the transition peaks of the radicals in solid hydrogen are well separated from those of parent molecules due to the sharpness of our spectra. Our recent results on spectroscopy and dynamics of methyl and ethyl radicals in parahydrogen crystals will be discussed.

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**Photodissociation Dynamics of Dicyclopropyl Ketone using Time-Resolved Fourier Transform Spectroscopy: Production of Allyl or Cyclopropyl Radicals?**

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The photodissociation dynamics of dicyclopropyl ketone at 193 nm has been studied using time-resolved Fourier transform emission spectroscopy. Dicyclopropyl ketone ( $\text{C}_3\text{H}_5\text{COC}_3\text{H}_5$ , or DCPK) is a symmetric ketone analogous to acetone, with a similar  $\text{S}_2 \leftarrow \text{S}_0$  absorption. At 193 nm, acetone undergoes sequential bond ruptures to form  $\text{CH}_3 + \text{CO} + \text{CH}_3$  with nearly unity quantum yield. The goals of the present study on photodissociation of DCPK are threefold: 1) determine the product channels, including isomeric form; 2) measure the disposal of energy into products; 3) describe the dissociation mechanism. Using time-resolved Fourier transform emission spectroscopy, we spectrally and temporally resolve the emission of the products in a room temperature cell environment. The highly multiplexed experiment provides time resolution of  $\sim 300$  ns with spectral resolution up to  $0.1 \text{ cm}^{-1}$  and spectral coverage of  $800 - 4000 \text{ cm}^{-1}$ . Our results show that DCPK dissociates to  $\text{C}_3\text{H}_5 + \text{CO} + \text{C}_3\text{H}_5$ . Rovibrational state distributions for the CO product show that  $\langle E_{\text{vib}} \rangle(\text{CO}) = 3.1 \text{ kcal/mol}$ , and

$\langle E_{\text{rot}} \rangle(\text{CO}) \geq 4 \text{ kcal/mol}$ . These distributions are significantly hotter than those in acetone dissociation, despite the fact that DCPK has twice as many vibrational modes. The time-resolved spectra of the  $\text{C}_3\text{H}_5$  fragment are consistent with the allyl radical, not the cyclopropyl radical, a result confirmed by radical trapping experiments with excess  $\text{Br}_2$ . To clarify the reaction mechanism, important stationary points on the potential energy surface have been characterized by density functional theory calculations. All of the results are consistent with a dissociation mechanism in which internal conversion to  $\text{S}_0$  is followed by ring opening of the cyclopropyl ligands. As the ring-opened  $\text{C}_3\text{H}_5$  ligands dissociate from the carbonyl fragment they become resonantly stabilized allyl radicals, liberating a total of  $\sim 62 \text{ kcal/mol}$  of energy. This isomerization energy (and a small exit barrier to CO elimination) accounts for the observation that the CO state distributions are much hotter than those observed in acetone dissociation, even though DCPK has twice as many vibrational modes and less energy available to products than acetone.

## The electric dipole moments of the $D^1\Pi$ state in HfS and the $b^3\Pi_1$ state in HfO.

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A laser ablation source combined with a time of flight mass spectrometer<sup>1</sup> has been used to determine the permanent electric dipole moments of some excited states in HfS and HfO. The apparatus has been used earlier<sup>2</sup> in a similar experiment. The key is to use the static electric field in the mass spectrometer to induce the first order Stark splitting from which the permanent electric dipole moment can be determined. By using a pulse amplified single mode ring-dye-laser this splitting is directly observable in the spectrum. The permanent electric dipole moment for the  $X^1\Sigma^+$  - ground state of HfO is known to be 3.431 D<sup>3</sup>.

In this work we have measured the first order Stark splittings of the  $D^1\Pi$  state ( $v=0,1$ ) in <sup>180</sup>HfS and the  $b^3\Pi_1$  state ( $v=0$ ) in <sup>180</sup>HfO, from which the dipole moments were determined to be 3.419(23), 3.480(25) and 2.678(29) D respectively. We have also compared the experimental results with *ab initio* calculations.

In the investigations of the  $D^1\Pi$  in HfS we noticed how a static electric field may give rise to "forbidden lines" e.g. the  $Q_{ee}$  and  $R_{ef}$  transitions from the  $X^1\Sigma^+$  ground state. These forbidden lines are the result of an electric field induced *e/f*-mixing of the two  $\Lambda$ -components in the  $^1\Pi$  state.

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## Sulfuric Acid Photochemistry in the Clouds of Venus

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A long-standing problem with the atmosphere of Venus is the evident stability of the planet's 96% CO<sub>2</sub> atmosphere, despite continuous irradiation with sunlight and efficient transport of fresh CO<sub>2</sub> to the region above the clouds. Our previous work<sup>1</sup> has shown that, in the presence of a sulfuric acid aerosol, CO can be converted to CO<sub>2</sub> by irradiation with a 193 nm ArF laser in a flow system. A minor mystery in these studies was the observation that the process either could produce SO<sub>2</sub>, as we had anticipated, or could remove SO<sub>2</sub> that was introduced as a mass spectrometric standard at a point some distance downstream from the irradiation cell.

Subsequent theoretical work<sup>2</sup> has shown that pure sulfuric acid does not absorb at 193 nm, so the primary process in the studies with pure sulfuric acid aerosols must have involved multiphoton absorption, due to focusing of the laser radiation by the small droplets.<sup>3</sup>

To avoid multiphoton processes, the present experiments used bulk samples of concentrated sulfuric acid instead of an aerosol and, instead of using mass spectrometry, the progress of photochemical reaction was followed by photometric monitoring of the conversion of trace amounts of dissolved Fe(II) to Fe(III). The irradiation was done with a 248 nm KrF laser, for better comparability with the HALIPP studies<sup>4</sup> of the photochemical conversion of SO<sub>2</sub> to sulfuric acid during the formation of acid rain. The results show that photochemical reactions in the sulfuric acid clouds of Venus are capable of affecting the composition of the atmosphere at high altitudes, by removing O<sub>2</sub> and CO and regenerating CO<sub>2</sub>. Major primary processes are the production of •SO<sub>3</sub><sup>-</sup> radical ions by photolysis of solvated SO<sub>2</sub>, and of •SO<sub>4</sub><sup>-</sup> radical ions by photolysis of complex ions containing Fe(III), if traces of iron salts are present. Secondary processes are mostly similar to those which lead to the formation of acid rain in Earth's troposphere. They result in removal of O<sub>2</sub> and the eventual formation of Caro's acid, H<sub>2</sub>SO<sub>5</sub>, which is a powerful, long-lived oxidizer, capable of oxidizing CO to CO<sub>2</sub> and of removing SO<sub>2</sub> introduced downstream of the irradiation zone in the aerosol experiments.

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A STEREODYNAMICS STUDY OF THE  $O(^1D)+HCl$  REACTIONV.Piermarini<sup>a</sup>, A. Laganà<sup>a</sup> and G.G. Balint-Kurti<sup>b</sup><sup>a</sup> Università di Perugia, Dipartimento di Chimica, Via Elce di sotto 8, 06100 Perugia, Italy<sup>b</sup> School of Chemistry, University of Bristol, Bristol, United Kingdom

State to state probabilities of the  $O(^1D)+HCl$  reaction were computed for a fairly wide range of energy. The efficiency of this reaction, that plays an important role in the modeling of the atmosphere since  $O(^1D)$  (produced by  $O_3$  when photodissociating) reacts with the halogenated idrogen to give OH and ClO radicals, depends on several factors.

It significantly depends on the collision energy as evidenced by the dependence of the branching ratio from that energy. It also depends on the initial orientation of the target HCl molecule that, contrary to the findings of ref. [1], moving from low to high collision energy tends to privilege collinear reactivity from the Cl side.

The dynamical study of the  $O(^1D)+HCl$  reaction has been performed on a potential energy surface fitted to ab initio values using a polynomial expansion in the bond-order variables [2]. To this end a time-dependent exact quantum technique was used [3].

Time dependent calculation on a different potential energy surface have been carried out by Bowman and collaborators [4].

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## An Atom-Bond Pairwise Additivity Approach for Calculation of Intermolecular Forces in Atom-Molecule Systems

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A new method is proposed for calculations of intermolecular interactions in van der Waals complexes which is of general applicability and gives accurate results with a negligible effort in terms of computing time. The method is based on correlation formulas between the polarizability of the interacting partners and the main interaction parameters. Our attention was originally addressed to spherical atom--closed shell atom systems [1,2,3] bound by typical van der Waals forces, where the attractive and repulsive component of the interaction were modeled in terms only of the polarizabilities of the interacting partners. This represented the foundation for a proper description of ion--atom [4] ion--ion [5], and open shell atom--closed shell particle systems [6,7], where in addition to van der Waals forces, additional interaction components operate.

The present work [8] is concerned with the extension of the method to systems involving diatoms or polyatomic molecules interacting with a closed shell atom. The basic idea is to consider the molecular size as determined by the bonds nearest to the approaching atom and to delocalize the dispersion centers on the molecule by using additively bond polarizabilities. The method, tested mainly on homonuclear diatomics-rare gas and simple hydrocarbon-rare gas complexes for which experimental and theoretical information is available, is used to make predictions for systems of higher complexity up to a graphite plane. This effort is worthwhile for an advanced and systematic study of phenomena like collisional alignment, broadening and shift of spectral lines of molecules in very different environments, steric effects in elementary processes, chemistry and physics of aggregates, transport properties in gas phase and physical absorption on surfaces. Moreover, as for atom--atom cases, the results of this work could be crucial for a proper representation of systems with increasing complexity where in addition to typical van der Waals forces, induction, electrostatic and chemical contributions can operate.

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## Experimental and theoretical study of charge exchange processes in ion-metastable rare gas atom collisions

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Ions and excited atoms or molecules play an important role in many high-energy systems, like plasmas or electrical discharges. However, since these species are both unstable, a direct study of relevant processes is rather difficult. The most effective way to observe and study collisions between ions and metastable rare gas atoms should be a crossed beam experiment. An apparatus of this type, already working in the laboratory of Trento for ion-molecule reaction studies, has been appropriately modified for this purpose.

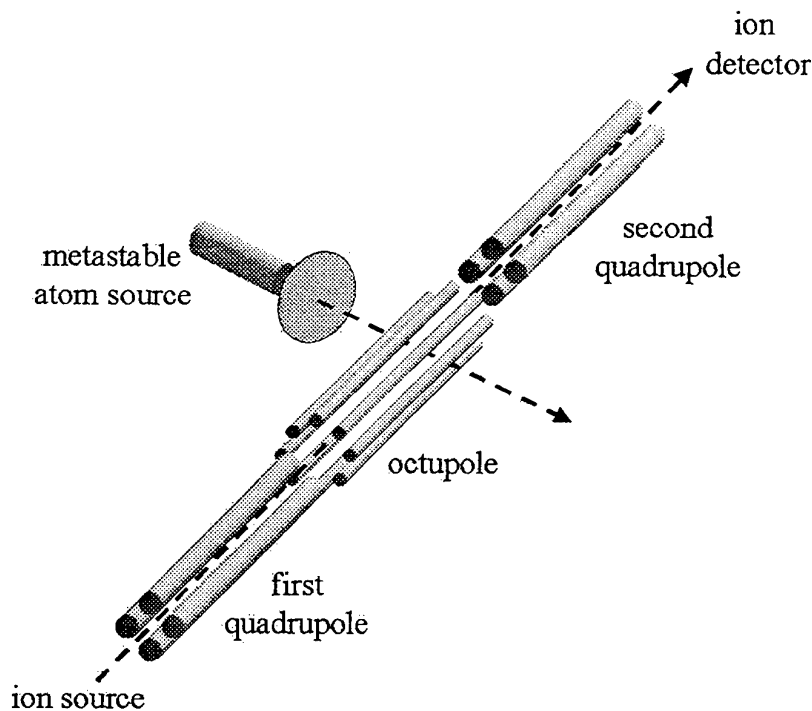
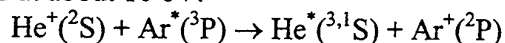


Figure 1 – Schematic view of the experimental set up

The apparatus, schematically sketched in the figure, consists of an ion source, a first quadrupole mass filter, an octupole trap, a second quadrupole mass filter and an ion detector. The target metastable rare gas atom beam is obtained by a supersonic continuous beam, with a d.c. discharge between nozzle and skimmer. The metastable atom beam crosses the ions confined by the octupole trap. The product ions are also trapped and can be detected after mass analysis in the second quadrupole filter.

The charge exchange process in collisions between  $\text{He}^+$  ions and metastable  $\text{Ar}^*(^3\text{P})$  atoms it has been observed at about 10 eV:



A theoretical work has been started in order to rationalize this observation, and the results will be presented at the meeting.

## Exploring the OH + CO $\rightarrow$ HOCO Reaction Pathway through Infrared Spectroscopy of the OH-CO Reactant Complex

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A hydrogen-bonded OH-CO complex has been identified along the reaction coordinate for the OH + CO  $\leftrightarrow$  HOCO  $\rightarrow$  H + CO<sub>2</sub> reaction. The infrared spectrum of this complex has been examined in the OH overtone region at 1.4  $\mu\text{m}$  using action spectroscopy, which relies on laser-induced fluorescence detection of OH ( $v=1$ ) fragments from vibrational predissociation. The strongest feature in the infrared spectrum is the pure OH overtone band of OH-CO at 6941.7  $\text{cm}^{-1}$ , shifted 29.6  $\text{cm}^{-1}$  to lower energy from the OH monomer transition. The rotational structure of this band is indicative of a parallel transition of a linear OH-CO complex having a  $P=3/2$  projection of the total angular momentum on the intermolecular axis, which arises from the unquenched electronic angular momentum of OH. The OH-CO binding energy,  $D_0 \leq 430 \text{ cm}^{-1}$ , is established from the quantum state distribution of the OH fragments following pure overtone excitation. In addition, combination bands involving the simultaneous excitation of OH stretch and intermolecular bend and/or spin-orbit excitation are observed 50 to 250  $\text{cm}^{-1}$  higher in energy than the pure overtone band. The combination bands with 51.1, 57.1, and 247.3  $\text{cm}^{-1}$  of intermolecular energy are attributed to geared bend and H-atom bend excitation, which are the modes that drive the transformation from OH-CO to HOCO. These combination bands exhibit rotational structures that are characteristic of perpendicular transitions ( $\Delta P = \pm 1$ ) to states with vibrational angular momentum arising from bending motions of the complex. The combination bands at the highest intermolecular energy lie in close proximity to the transition state leading to the HOCO intermediate. The experimentally determined geometry, bond length, binding energy, OH spectral shift, and vibrational frequencies are all consistent with *ab initio* predictions for the OH-CO complex. Further characterization of the direct reaction path leading to HOCO is ongoing through spectroscopic experiments and analysis.

Photodissociation Dynamics of the Low Lying Electronic States of CH<sub>2</sub>Cl  
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The photodissociation dynamics of the CH<sub>2</sub>Cl radical are investigated in the region of 311 nm to 214 nm using REMPI product detection combined with velocity map photofragment ion imaging. Perpendicular and parallel transitions are observed at 311 - 247 nm and 245 - 214 nm, respectively. The perpendicular and parallel transitions are attributed to excitations to the <sup>2</sup>A<sub>1</sub> and the <sup>2</sup>B<sub>1</sub> valence states, respectively, in agreement with recent *ab-initio* calculations. A strong enhancement of the perpendicular transition is observed due to excitation of vibrationally excited CH<sub>2</sub>Cl. The anisotropy of the products, such as Cl, CH<sub>2</sub> and H, reflects the nature of the excited state being accessed. The participation of valence and Rydberg states will also be discussed.

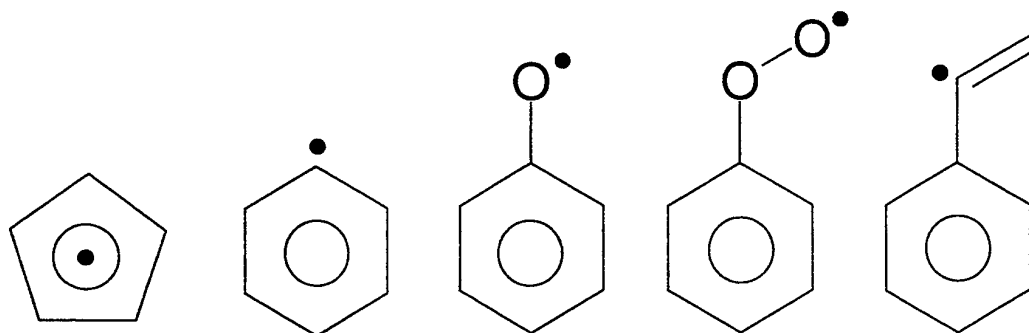
## Optical Spectroscopy of Aromatic Radicals

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### Abstract:

Simple aromatic radicals: phenyl, phenoxy, cyclopentadienyl, phenyl peroxy, phenyl vinyl were prepared using several generation methods and a variety of precursors and stabilized for spectral scrutiny by matrix isolation. Simultaneous spectral observations in the IR and UV-Vis, IR and Raman, UV-Vis and luminescence, and IR/ESR lead to exceedingly sharp and detailed and highly reliable vibrational and electronic spectral fingerprints of radicals. With the aid of quantum chemical computations, use of several isotopic labels and polarization spectroscopy performed on photooriented samples we were able to detect and assign energies and symmetries for nearly all vibrational and doublet electronic transitions in the 100-50,000  $\text{cm}^{-1}$  region. The use of internal standards allowed for determination of cross-sections and extinction coefficients. Several controversial issues were settled regarding spectral assignments, the identity of the investigated species, and various aspects of the reactivity. The results provide reliable basis for advancement in analytical and kinetic studies in combustion, atmospheric and biological chemistry. They could also serve as the test cases in fine tuning of existing quantum-chemical approaches and development of new computational methods for precise predictions of structures, energetics and reactivity for open-shell molecules.



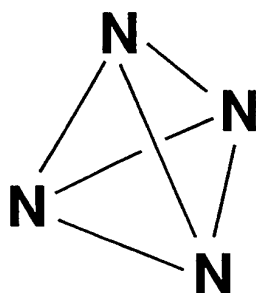
## Tetrazete ( $N_4$ ). Can It Be Prepared and Observed?

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### Abstract:

Reactions of nitrogen radicals in plasma generated by microwave or electrical discharge in gaseous  $N_2$  produce unusual molecules. When such plasma is quenched on a cold spectroscopic window (6.2 – 35 K) and resulting matrix is examined by IR and UV-Vis absorption spectroscopies, we observe a weak infrared transition at  $936.7\text{ cm}^{-1}$  in samples prepared from  $^{14}N_2$ . This band shifts to  $900.0\text{ cm}^{-1}$  when  $^{15}N_2$  is used. Both peaks do not correlate with any other features in the spectra and are best explained as originating from tetrahedral tetrazetes ( $N_4$ ). Their positions are compatible with quantum chemical estimates for  $^{14}N_4$ , at  $936.0\text{ cm}^{-1}$  and  $^{15}N_4$ , at  $904.4\text{ cm}^{-1}$ .





### Dynamics of Cl<sub>3</sub> radical-molecule complex studied on LiF (001) surface.

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Photodissociation of chlorine adsorbed on a LiF (001) surface at 25-70 K has been investigated by means of angularly-resolved resonantly-enhanced multiphoton ionization spectroscopy (REMPI). The translational-energy distributions and angular distributions for forming Cl(g) photofragments were determined. Photolysis was performed employing 351 nm radiation, with laser pulse energies of 0.3-1.2 mJ/cm<sup>2</sup>. A peak in the translational energy of Cl(g) at about 0.4 eV was identified as being due to the direct photodissociation of the Cl<sub>2</sub>(ad) molecule by 3.5 eV photons. Particular interest attached to the observation of a further channel (termed "A") for photodissociation leading to Cl(g) with translational energy peaking at ~1 eV and extending to 1.5 eV. The available photon energy renders it highly unlikely that this "high-energy" Cl(g) originates in Cl<sub>2</sub>(ad). Channel A had the same linear dependence of Cl-atom flux on laser pulse-energy as did the lower energy (0.4 eV) channel, termed "B", but differed from it in exhibiting a slow approach to steady state. It appears that channel A requires the prior build-up of Cl(ad) concentration due to the photodissociation of Cl<sub>2</sub>. It is proposed that this leads to the formation of a steady-state concentration of Cl<sub>2</sub> ··Cl (or Cl<sub>3</sub>) which when photolyzed yields high-energy Cl(g) via channel A. Channel A exhibits a distinctive angular distribution at low coverage and a characteristic Cl<sup>\*</sup>/Cl ratio, as compared with channel B. The suggested mechanism for channel A is Cl<sub>2</sub> ··Cl + hν → Cl<sub>3</sub><sup>\*</sup> →

Cl<sub>2</sub> • Cl → Cl<sub>2</sub> +  $\vec{\text{Cl}}$  (where <sup>\*</sup> is a bound electronically excited state and • represents repulsion in the lower electronic state to which Cl<sub>3</sub><sup>\*</sup> reverts). This mechanism is interpreted in terms of an extensive diatomics-in-molecules (DIM) model for the trichlorine radical, shown to be in agreement with high-level *ab initio* multireference internally-contracted configuration interaction (MRCI) calculations and to be consistent with the observations.

# DMSO TROPOSPHERIC DEGRADATION IN THE GAS PHASE:: KINETIC AND PRODUCTS OF THE REACTION OF Cl – DMSO

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The atmospheric oxidation of dimethylsulfide ( $\text{CH}_3\text{SCH}_3$ , DMS), emitted from marine phytoplankton, has been extensively studied due to its connection with the production of sulphuric acid which has the ability to contribute to aerosol formation and growth in the remote marine environment <sup>1,2</sup>.

The addition of OH to DMS to form the  $\text{CH}_3\text{S(OH)CH}_3$  adduct and further reaction with  $\text{O}_2$  is also considered as the production source of DMSO in the atmosphere. DMSO is also found in the sea water as a result of bacterial transformation of DMS but this is not expected to represent a direct source since it is highly soluble in the liquid phase <sup>3,4</sup>.

The fate of DMSO in the atmosphere is poorly understood. Its removal from the gas phase may be due to a combination of heterogeneous processes and homogeneous reactions with OH,  $\text{NO}_3$ ,  $\text{O}_3$  and Cl atoms.

Since global average estimates of Cl atoms concentrations range from  $10^3$  to  $10^4$  atoms  $\text{cm}^{-3}$ , the effect on the removal of DMSO should be evaluated and compared to that of the OH-DMSO reaction <sup>5</sup>, presumably the most relevant sink.

In the present study, gas-phase rate constants for the reaction of Cl atoms with DMSO have been obtained for a range of temperature between 274 and 335K and for a range of pressures from 0.5 to 3.0 torr.. The experiments have been carried out using the discharge flow-mass spectrometry technique. All the kinetics measurement were performed under pseudo-first-order kinetic conditions in DMSO. Rate constants for this reaction are showed in table I. ( $\text{CH}_3\text{SOCH}_2\text{Cl}$ ) was detected as product of the reaction, showing an addition mechanism.  $\text{CH}_3\text{SOCl}$  and  $\text{CH}_3\text{Cl}$  were also positively detected with profiles increasing with time. These observations suggest the cleavage of C –S bond in the adduct. Furthermore the reaction  $\text{ClO} + \text{DMSO} \rightarrow$  Products was also studied. Due to the low reactivity and DMSO vapor pressure only an upper limit of  $k \leq 6 \times 10^{-14}$   $\text{molecule}^{-1} \text{cm}^3 \text{s}^{-1}$  could be measured. The high kinetic rate constant measured for Cl – DMSO reaction show that may be relevant in the DMSO removal in the marine boundary layer.

**Table I. Absolute rate constants in  $\text{molecule}^{-1} \text{cm}^3 \text{s}^{-1}$  for the reaction of Cl with DMSO.**

P= 0.5 Torr	P= 1 Torr			P= 3 Torr
T= 25° C	T= 0° C	T= 25° C	T= 62° C	T= 25° C
$(1.6 \pm 0.2) \times 10^{-11}$	$(1.6 \pm 0.2) \times 10^{-11}$	$(1.7 \pm 0.3) \times 10^{-11}$	$(1.4 \pm 0.3) \times 10^{-11}$	$(2.0 \pm 0.3) \times 10^{-11}$

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## Representation in Hyperspherical and Related Coordinates of the Potential Energy Surface for Open-shell Tetratomic Reactions

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Open-shell molecular reactions like  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$  and  $\text{CN} + \text{H}_2 \rightarrow \text{HCN} + \text{H}$  are currently under extensive experimental and theoretical study because of their prototype nature in the field of chemical reaction dynamics and are rapidly becoming the four-atom equivalents of the much investigated  $\text{F} + \text{H}_2$  reaction.<sup>1</sup> Theoretical studies on the dynamics started with the development of potential energy surfaces by ab initio means and with a series of quasiclassical trajectory and transition state theory investigations using the ground state surface.<sup>2</sup> As for the  $\text{F} + \text{H}_2$  reaction also here a role is played by excited surfaces arising out of the open shell nature of OH and CN.<sup>3</sup> Grid points and fits for the PES are developed from a recently proposed tetratomic hyperspherical coordinate approach.<sup>4</sup> The results of experimental and previous theoretical works<sup>5</sup> are compared with the prediction of three different ab initio potential energy surfaces.

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Experimental and Modeling Studies of N<sub>2</sub>O- and NO<sub>2</sub>-Containing Flames: The Detection of Free Radicals by Laser Spectroscopy and Molecular Beam-Mass Spectrometry

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**ABSTRACT**

Experimental and chemical modeling studies of 30-Torr, H<sub>2</sub>/N<sub>2</sub>O/Ar, NH<sub>3</sub>/H<sub>2</sub>/N<sub>2</sub>O/Ar, and H<sub>2</sub>/N<sub>2</sub>O/NO<sub>2</sub>/Ar flames are performed to test and refine a detailed chemical mechanism developed in our laboratory. This mechanism consists of 103 reactions and 22 species and is denoted VS-modified-2. Flame temperatures are measured with a coated, thin-wire thermocouple and by OH and NH laser-induced fluorescence (LIF). Species concentration profiles of H<sub>2</sub>, NH<sub>3</sub>, NO<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub>, H<sub>2</sub>O, NO, O<sub>2</sub>, O, H, NH and OH are recorded using molecular beam/mass spectrometry, LIF, or both. The experimental species concentrations are compared to those generated with PREMIX, a one-dimensional, laminar, flame code, using the measured temperature profile and VS-modified-2 mechanism as input. Overall, the PREMIX calculations predict very well the major, species concentrations throughout each flame. For the H<sub>2</sub>/N<sub>2</sub>O/Ar flame, the postflame, O<sub>2</sub>, OH, and NO concentrations decrease by approximately 90, 45, and 32%, respectively, with the addition of ~4% NH<sub>3</sub>. This decrease is predicted rather well by the PREMIX calculations, which show a decrease in O<sub>2</sub>, OH, and NO by approximately 90, 55, and 40%, respectively. The shapes of the modeled O<sub>2</sub>, NO, O, H, and OH profiles for the H<sub>2</sub>/N<sub>2</sub>O/Ar flame agree well with those observed experimentally, and the modeled OH profile for the H<sub>2</sub>/N<sub>2</sub>O/NO<sub>2</sub>/Ar flame predicts an observed peak at approximately 3 mm above the burner surface. This peak is attributed to the competition between the NO<sub>2</sub>+H=NO+OH reaction, which produces OH, and the H<sub>2</sub>+OH=H<sub>2</sub>O+H reaction, which consumes it. Rate and sensitivity analyses of these flames are presented discussed.

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## Femtosecond Dynamics of Diphenylpolyenes in Solution:

### A Fluorescence Up-Conversion Study

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The short time dynamics of the  $S_1$ -photoisomerization of diphenylpolyenes, in particular of *trans*-stilbene and *E,E*-diphenyl-(1,3)-butadiene, continue to be the subject of controversial discussion. [1-6] One of the key questions addresses the time scale of intramolecular vibrational energy redistribution (IVR) in conjunction with the validity of employing statistical rate theory to calculate rate constants of the photoisomerization.

We present new experimental results from fluorescence up-conversion studies confirming the view that, in liquid solution after excitation at 266 nm, IVR is complete on a time scale of a few hundred femtoseconds. The subsequent time evolution critically depends on the electronic level structure of the diphenylpolyene and is governed by competing interstate coupling, vibrational energy relaxation and photoisomerization of the vibrationally hot molecule, until finally, after a couple of picoseconds, the regime of a thermal reaction in the  $S_1$ -state is reached. For the case *trans*-stilbene, of rate constants of the vibrationally hot and thermal molecule are perfectly described by statistical rate theory employing a new harmonic model based on *ab initio* calculations of the  $S_1$ -state.

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## Spectroscopy and dissociation of acetylene in the *np gerade* Rydberg states

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The high-lying *gerade* Rydberg states of acetylene have not been measured in the resonance enhanced multiphoton ionization (REMPI) up to now. One of the reasons is supposed for the *gerade* Rydberg states to be very short-lived due to fast dissociation and to be inefficient to be resonantly ionized.

In the present study, the *np gerade* Rydberg states of acetylene were tried to detected and characterized by using various spectroscopic techniques to measure one-color resonant multiphoton ionization spectra, two-color REMPI mass spectra, emission spectra and laser induced fluorescence (LIF) spectra in the two-photon energy region of 72000-92000  $\text{cm}^{-1}$ . The TOF mass spectrometer used in this study has been described in detail previously.<sup>1)</sup>

The  $3p\ ^1\Sigma_g^+$  and  $^1\Delta_g$  Rydberg states were confirmed to exist between 72000 and 77000  $\text{cm}^{-1}$ , which accords with the observation by Ashfold et al.<sup>2)</sup> One of the upper levels, which are located at 82561.5  $\text{cm}^{-1}$ , are found to be exceptionally narrow in linewidth and the rotational analysis has successfully been performed. The measured spectrum fits well with the simulation for a  $\Delta$ - $\Sigma$  transition which suggests that the upper level is the  $4p\ ^1\Delta_g$  Rydberg state. All the *gerade* Rydberg states measured in a higher energy region are found to be predissociative and the emission due to  $\text{C}_2\ d^3\Pi_g - a^3\Pi_u$  Swan band was observed always under the two-photon resonance conditions of acetylene to prepare the *np gerade* Rydberg states. In the LIF spectrum measured by monitoring  $\text{C}_2\ d^3\Pi_g - a^3\Pi_u$  Swan band emission, higher members of *np*  $^1\Sigma_g^+$  and  $^1\Delta_g$  Rydberg series ( $n > 4$ ) were identified for the first time.

The predissociative lifetimes for the *np gerade* Rydberg states are estimated from the spectral bandwidths. The lifetimes of the *gerade* Rydberg states are found to vary over 0.1-2 ps but to be not so short as previously expected. The predissociation mechanisms of acetylene to form  $\text{C}_2$  in the  $d^3\Pi_g$  state will be discussed.

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## LASER SPECTROSCOPY OF FeN AND FeC IN THE VISIBLE REGION

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Two iron-containing diatomic radicals of FeN and FeC have been studied using laser spectroscopic methods of laser-induced fluorescence (LIF), dispersed fluorescence (DF), and stimulated emission pumping (SEP). These transition-metal mononitride and monocarbide radicals were generated by the reactions of laser-ablated Fe atoms with ammonia and methane, respectively, 3% diluted in 2.5 atm helium carrier gas and studied spectroscopically at 0.04-0.06  $\text{cm}^{-1}$  resolution under supersonic jet-cooled conditions.<sup>1)</sup>

We have reported the first gas-phase spectroscopic study of iron mononitride radical (FeN).<sup>2)</sup> The LIF excitation spectrum was measured between 16300 and 21600  $\text{cm}^{-1}$ , and the rotational analyses have been performed for about 25 vibronic bands. The  $\Omega$  value of the ground state has been determined to be 5/2, which could be the spin-orbit component of  $^2\Delta(\dots 1\delta^3 9\sigma^2)$  or  $^4\Pi(\dots 1\delta^3 9\sigma^1 4\pi^1)$ . The excited states in the visible absorption region show very complicated rovibronic structures due to heavy perturbations. The excited states measured are classified into five  $\Omega=5/2 - X \Omega=5/2$  band systems.

The LIF spectrum of iron monocarbide radical (FeC) was recorded in the 15000-23800  $\text{cm}^{-1}$  region. The rotational analyses have been carried out for 46 vibronic bands. About 35 band among them have been observed for the first time, while the other 11 bands were previously recorded at 0.2  $\text{cm}^{-1}$  resolution by Balfour et al.<sup>3)</sup> The energy separation between the  $\Omega=3$  and 1 spin components of the  $X^3\Delta_i$  state has been determined with the observation of some mixed rotational levels prepared from both the  $X^3\Delta_3$  and  $X^3\Delta_1$  states. As the energy separation between the  $\Omega=3$  and 2 spin components of the  $X^3\Delta_i$  state has also been determined by Fujitake et al.<sup>4)</sup> all the excited vibronic levels could be successfully placed on the same energy scale. In the visible spectrum, we could characterize five electronic states for which the Hund's case (a) labels are possible, namely, three  $^3\Delta$ , one  $^3\Pi$ , and one  $^1\Delta$  states.

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## THREE-BODY RECOMBINATION OF ULTRACOLD OPEN-SHELL ATOMS

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In three-body recombination the formation of a molecule results from the collision of three initially separated atoms. Three-body recombination is important in the context of atoms trapping and cooling as it reduces the lifetime of ultracold trapped atoms [1], and can become relevant either at relatively high density, or when the two-body inelastic processes are absent. Particular attention must be paid to formally deriving collisional rate events when the colliding particles are identical bosons or fermions. Due to the Wigner threshold laws, in the ultracold regime  $T \sim \text{nK}$  only one or at most a few partial waves contribute to the recombination rate, and an exact quantum mechanical solution of the problem might be within the power of current computer technology.

We approach the problem using hyperspherical coordinates. Within the hyperspherical framework [2], the hyperquantization algorithm [3] is a method that allows for an efficient solution [4] of the fixed-hyperradius eigenvalue problem. The algorithm is currently being extended to treat the recombination process in the ultracold limit. This extension requires the evaluation of the channel coupling up to few hundreds Bohr. Also, the scattering equation must be propagated out to hundreds thousand Bohr in order to reach convergence in the scattering matrix. Elastic and inelastic collision rates at ultracold temperatures are extremely sensitive not only to the long-range van der Waals tail of the internuclear potential, but also to the short-range chemical-bonding region of the potential. The importance of short-range contributions to the interaction potential, like the three-body Axilrod-Teller term, will thereby be investigated. The ro-vibrational distribution of the molecules produced via recombination will also be discussed.

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## Reaction and Vibrational Relaxation in Collisions of H Atoms with Vibrationally Excited H<sub>2</sub>O

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The removal of H<sub>2</sub>O molecules from their |04><sup>-</sup> vibrational state in collisions with H atoms can occur both by *reaction*, producing OH(*v* = 0) + H<sub>2</sub>, and by non-reactive *relaxation*. We report an experimental measurement of the fraction (*f*<sub>reac</sub>) that occurs by reaction. The value of *f*<sub>reac</sub> is determined by comparing the yields of OH from three experiments in which the same concentration of H<sub>2</sub>O(|04><sup>-</sup>) is prepared by overtone absorption of pulsed laser radiation and OH(*v* = 0) is produced: (i) solely by the H + H<sub>2</sub>O(|04><sup>-</sup>) reaction; (ii) solely by the photodissociation of H<sub>2</sub>O(|04><sup>-</sup>) at 266 nm; and (iii) both by the photodissociation of H<sub>2</sub>O(|04><sup>-</sup>) and by the subsequent reaction of a fraction of the remaining H<sub>2</sub>O(|04><sup>-</sup>) with H atoms. Analysis of these experiments shows that *f*<sub>reac</sub> = (0.34 ± 0.11). The experimental results are compared with the results of two kinds of scattering calculations performed on a potential energy surface developed recently, specifically with this problem in mind. Using the vibrational coupled-channel infinite-order-sudden (VCC-IOS) method, rate coefficients have been calculated for individual vibrationally inelastic processes and then summed to find the rate coefficient (*k*<sub>relax</sub><sup>H</sup>) for total non-reactive relaxation from the |04><sup>-</sup> state. The quasiclassical trajectory (QCT) method has been used to calculate the rate coefficient (*k*<sub>reac</sub>) for reaction between H atoms and H<sub>2</sub>O(|04><sup>-</sup>). Both the calculated rate coefficient (i.e., *k*<sub>relax</sub><sup>H</sup> + *k*<sub>reac</sub>) for total loss from H<sub>2</sub>O(|04><sup>-</sup>) and the calculated branching ratio, *f*<sub>reac</sub> = *k*<sub>reac</sub>/(*k*<sub>relax</sub><sup>H</sup> + *k*<sub>reac</sub>) = 0.38, are in quite good agreement with the experimental values.

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## State-to-State Cross-Sections for Rotational Energy Transfer in Collisions between NO and He and NO and Ar

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A crossed molecular beam apparatus with two pulsed supersonic sources that can be rotated independently of each other has been used to study the transfer of energy in collisions between NO and Ar and NO and He. Expansion of mixtures of NO in neon through one nozzle ensures that the NO is cooled into its lowest rotational levels and predominantly into the lower  $\Omega = 1/2$  spin-orbit component of the  $X^2\Pi_{\Omega}$  electronic ground state. This beam crosses a second beam consisting of He or Ar atoms. Laser-induced fluorescence spectra of NO are recorded in the (1,0) band in the  $A^2\Sigma^+ - X^2\Pi_{\Omega}$  system with and without the second beam on. The difference in these two spectra directly reflects the distribution over final states following rotational energy transfer.

Two sets of results will be reported. Firstly, we shall report the variation of cross-sections for transfer from the narrow, initial, distribution of states to the final distribution deduced from the LIF spectra at several well-defined collision energies in the range of 250 to 1000  $\text{cm}^{-1}$ . Secondly, we shall present excitation functions (cross-sections versus collision energy) for transfer between defined states; i.e.  $\Omega = 1/2, J_{\text{initial}} = 1/2 \rightarrow \Omega = 1/2, J_{\text{final}}$ .

Finally, we expect to be able to present preliminary results from similar experiments on rotational energy transfer in collision between  $\text{C}_2\text{H}_2$  and He, and  $\text{C}_2\text{H}_2$  and Ar,

# **Total and State-to-State Rate Coefficients for Transfer of OH( $X^2\Pi_{3/2}$ , $\nu = 1$ , $J$ ) in Collisions with He, Ar and N<sub>2</sub>**

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In extended infrared-ultraviolet double resonance (IR-UVDR) experiments, we have measured rate coefficients for rotational energy transfer in collisions between OH radicals in selected spin-orbit, vibrational and rotational states in collisions with He, Ar and N<sub>2</sub>. OH radicals are generated by 266 nm photolysis of HNO<sub>3</sub> contained in a dilute mixture with the 'collisional gas'. OH radicals are then promoted to a selected rotational state in the  $X^2\Pi$ ,  $\Omega = 3/2$ ,  $\nu = 1$  vibronic level using a pulsed, tunable infrared laser source. The subsequent fate of these species is followed using delayed laser-induced fluorescence (LIF) in the (1,1) band of the  $A^2\Sigma^+ - X^2\Pi_{\Omega}$  system. Two kinds of experiment are performed. First, the frequency of the UV probe laser is fixed to correspond to an absorption line from the  $\nu = 1$ ,  $J$  level that is populated by the absorption of the IR pump and the time delay between pump and probe is systematically varied. The analysis of these experiments yields rate coefficients for total removal from the selected initial state. Examples of such rate coefficients are given in the Table. Second, the delay between the pulses from the pump and probe lasers is fixed and the frequency of the probe laser is scanned to record a LIF spectrum. From the intensities of the lines in the spectrum, one can deduce the relative populations in the states populated by collisions and hence the state-to-state rate coefficients for transfer between the chosen initial state and a range of final states. By choosing a short delay between the photolysis pump generating the OH radicals and the IR pump laser, it is possible to obtain information about collisional transfer from rotational levels beyond those which are significantly populated in a thermal distribution at room temperature.

**Rate coefficients ( $k / 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for total transfer from the designated levels in collisions with He, Ar and N<sub>2</sub>**

	$J = 3/2$	$J = 9/2$	$J = 11/2$	$J = 15/2$	$J = 17/2$
He	1.96±0.16	2.07±0.19	1.80±0.08	1.54±0.05	1.28±0.06
Ar	1.36±0.16	3.04±0.08	2.39±0.04	1.39±0.05	1.20±0.08
N <sub>2</sub>	4.44±0.18	4.52±0.30	4.38±0.17	3.32±0.22	2.10±0.10

## Electron-induced chemistry of 5-Chlorouracil

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The mechanism of dissociative electron attachment to 5-Chlorouracil (UCI) is studied by ab initio calculations. Temporary electronic states of the 5-Chlorouracil radical anion associated with electron attachment to different valence orbitals have been investigated at the static-exchange level using the complex absorbing potential method. This approach yields the complex resonance energies  $E + i\Gamma/2$  of the examined metastable states, i.e., the energies *and* the autodetachment lifetimes  $\tau = \hbar/\Gamma$ . One  $^2A'$  ( $\sigma^*$ ) and three  $^2A''$  ( $\pi^*$ ) states of the temporary  $\text{UCI}^-$  anion have been identified, and a cut through the complex potential energy surfaces of these four states defined by the C-Cl bond distance has been studied.

Our results show that only the  $\sigma^*$  state is dissociative in nature, whereas the  $\pi^*$  states are bound with respect to dissociation of the C-Cl bond. However, dissociation is improbable, if the  $\sigma^*$  state is formed directly, since its autodetachment lifetime is very short at the geometry of the neutral.

Dissociative electron attachment seems only possible, if initially the  $1^2A''$  or  $2^2A''$  states are formed which both show appreciable autodetachment lifetimes and cross the  $\sigma^*$  state at elongated C-Cl bond lengths in the form of a conical intersection. Since any out-of-plane ( $a''$ ) vibration will couple the  $^2A''$  and the  $^2A'$  states, at the conical intersection the  $\pi^*$  anion can efficiently 'hop' onto the dissociative  $\sigma^*$  surface at a geometry where the autodetachment lifetime of the  $\sigma^*$  state is already much longer. We have found similar situations in dissociative attachment to (substituted) Chlorobenzene, and thus, the described mechanism may be prototypical for a large class of halogen substituted  $\pi$ -systems.

The Spectroscopy of Gas-Phase  $\text{Pt}_2\text{C}_2$ 

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Up to very recently YCC was the only metal- $\text{C}_2$  molecule for which high resolution spectral information was available. Recently we have recorded numerous band systems in the blue/green region of the visible spectrum which we believe to be  $\text{Pt}_2\text{C}_2$  or possibly  $\text{PtC}_2$  using LIF and dispersed LIF spectroscopy. The LIF excitation spectrum of the  $0_0^0 \tilde{A}^2A_1 - \tilde{X}^2A_1$  band system near  $18185 \text{ cm}^{-1}$  is presented in **Figure 1**.

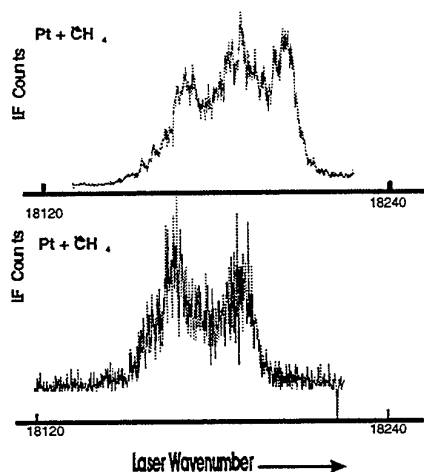


Fig. 1. Low Resolution LIF of  $\text{Pt}_2\text{C}_2$  of  $\text{PtC}_2$ .

These spectra were recorded using a pulsed dye laser system at a resolution of  $\approx 0.05 \text{ cm}^{-1}$ . Much of what appears to be “noise” is actually rotational structure. The presence of the Q-branch for the  $^{13}\text{C}(I=1/2)$  demonstrates that the molecule is “T-Shaped” with equivalent Fermi-Dirac nuclei. Additional excitation bands are observed at  $18422 \text{ cm}^{-1}$ ,  $18665 \text{ cm}^{-1}$  and  $18874 \text{ cm}^{-1}$ , which we tentatively assigned as a progression in the excited state asymmetric stretch mode. A progress report will be given.

**Millimeter-wave and Infrared Spectroscopy Combined with Pulsed-jet Expansion  
Technique for the Detection of the Transitions of Molecules**

**Produced by UV Laser Photolysis**

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To observed the rotational spectra of free radicals produced in a supersonic jet expansion by 193 nm ArF excimer laser photolysis by a time-resolved millimeter-wave spectrometer was set up with backward-wave oscillator as a radiation source. The SO radical produced by the photolysis of  $\text{SOCl}_2$  was detected as a test. The technique was applied to observed the vinyl radical with the UV photolysis of vinylbromide, and the pure rotational line split into four components, by spin-rotation and tunneling effects, have been detected.

The similar technique has been applied in the infrared region, to observed the jet cooled  $\text{Fe}(\text{CO})_x$  ( $x=1,3$ ) radicals produced in a supersonic jet expansion by 193 nm ArF excimer laser photolysis of iron pentacarbonyl  $\text{Fe}(\text{CO})_5$  with the time-resolved infrared diode laser spectroscopy. The rovibrational lines of  $\square\text{FeCO}$  near the  $\nu_1$  band origin were observed split into triplet due to the  $^3\Sigma^-$  electronic ground state. The hot band transitions of  $\nu_1$  from the  $\nu_2$  bending state has been also observed. Each rotational lines was split into sextet due to the  $\Lambda$ -type doubling as well as the spin-spin interaction, because of the vibronic interaction between the lower located electronic state.

The jet-cooled spectra of the  $\nu_3$  band of  $\text{Fe}(\text{CO})_2$  have been observed split into triplet due to the  $^3\Sigma_g^-$  electronic ground state. Missing spin components were observed for each rovibrational lines due to the spin statistics of the C and O nuclei confirming that  $\text{Fe}(\text{CO})_2$  has a linear structure with  $D_{\square h}$  symmetry.

$\square\square$ The rotational spectra of FeCO radical in the ground and  $\nu_2$  bending states has been also observed in the millimeter-wave region.

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## Fourier Transform Emission Spectroscopy of the $B^2\Sigma^+ - X^2\Sigma^+$

### Transition of the $\text{PN}^+$ Ion

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Ultraviolet emission spectrum of the  $B^2\Sigma^+ - X^2\Sigma^+$  transition of the  $\text{PN}^+$  ion has been observed around  $31,000\text{ cm}^{-1}$  at a resolution of  $0.05\text{ cm}^{-1}$  by a Bruker IFS20HR Fourier transform spectrometer. Rotationally resolved spectrum of the  $\text{PN}^+$  ion, produced by ac discharge of the  $\text{PCl}_3$ ,  $\text{N}_2$ , and He gas mixture, was recorded for more than 10h accumulating the interferogram 1600 times. A monochromator was placed just before a photomultiplier to work effectively as an optical filter with a band width of about  $200\text{ cm}^{-1}$  omitting strong emission of the  $\text{N}_2$  molecule.

The (0,0) band lines, split into doublet due to the spin-rotation interaction, were assigned to the *R*- and *P*-branch lines of the *N* quantum number up to 35 [1]. The determined band origin  $\nu_0 = 31,058.9963\text{ (81)}\text{ cm}^{-1}$  is consistent with the previous results with low resolution [2]. The (1,0) and (0,1) bands also have been measured, but the  $(\text{PNCl}_2)_3$  molecule was used Instead of  $\text{PCl}_3$  to avoid the very strong emission of  $\text{N}_2$  located close to these bands.

The rotational, centrifugal distortion, and spin-rotation constants for both electronic states were determined as well as the vibrational frequencies. The  $B^2\Sigma^+$  state has much weaker bond than the  $X^2\Sigma^+$  ground state, because the bond length of the  $B^2\Sigma^+$  state ( $0.157\text{ \AA}$ ) is longer by  $0.076\text{ \AA}$  than that of the ground state. This is also the case for the force constant; that ( $k = 2.90\text{ mdyne/\AA}$ ) for the  $B^2\Sigma^+$  state is by about 70 % smaller than that of the ground state. Present results agree with the *ab initio* calculations which predict a shallow minimum for the  $B^2\Sigma^+$  state due to an avoiding crossing of PES [3].

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[3] *Chem. Phys. Lett.* , **120**, 383 (1988).

## Complications in Gas Phase Radical + Radical Combination Reactions: Pertinent Structural and Energetic Parameters for Bimolecular Formation and Unimolecular Removal Processes

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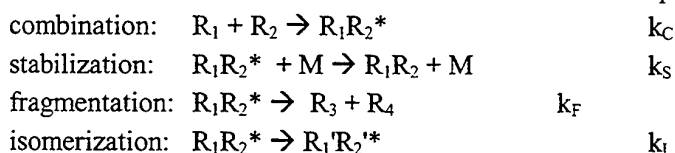
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The gas phase combination of free radicals, important in combustion and atmospheric chemistry, is frequently modeled using simple hard sphere collision partners. This assumption does not account for energetic and structural factors that determine the rate coefficient for the **formation** of the combination product and subsequent chemical processes that may **remove** the combination product. The later is the result of the exoergicity of the combination reaction; the chemically activated species must be collisionally stabilized to prevent unimolecular fragmentation and/or isomerization.

An abbreviated scheme which includes formation and removal processes is



The pressure dependence for the apparent rate coefficient for combination,  $k_C$  (as determined from the production of  $R_1R_2$ ) is determined by the relative magnitudes of  $k_S$  (vibrational energy transfer probabilities) and the unimolecular steps,  $k_F$  and  $k_I$ . When  $M$  is a weak collider a system of coupled differential equations for each active energy level must be solved.

We have studied the formation of butane (B), 1-butene (1B) and 1,3-butadiene (13B) from the self- or cross- combination of vinyl ( $C_2H_3$ ) or ethyl ( $C_2H_5$ ) radicals:  $C_2H_3 + C_2H_3$ ,  $C_2H_5 + C_2H_5$  and  $C_2H_3 + C_2H_5$ . Vinyl and ethyl radicals were produced by excimer laser photolysis (248 nm or 193 nm) of  $C_2H_3I$ ,  $C_2H_5COC_2H_5$  and  $C_2H_5COC_2H_3$ . The reaction products were identified and quantified using a sensitive gas chromatograph and mass spectrometer. The study covered a pressure range from approximately 2 Torr to 500 Torr at 298 K. Although  $k_C$  for B formation did not exhibit a pressure dependence the formations of 1B and 13B did; the yield of 13B at 2 Torr was reduced to less than 15% of its high pressure value. The product analysis at very low pressures also indicated the formation of cyclobutene and 1,2-butadiene; these products ( $C_4H_6$  isomers) were not present at high pressures. For the cross combination, the yield of 1B decreased with decreasing pressure and the first reported value for  $k_C$  was found to be  $6.5 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . Products resulting from fragmentation of allylic C-H and C-C bonds were also observed at low pressure.

The results of these experiments and model weak collider/RRKM calculations were used to determine energetic and structural parameters for processes that must be included in the mechanism for the self- and cross-combination of  $C_2H_5$  and  $C_2H_3$  radicals. An energy correlation for  $k_C$  (ranging from  $7 \times 10^{-12}$  to  $1.5 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ) is presented; collision rate theory predicts  $k_C$  within a small range of around  $2 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . The new energy correlation is used to predict  $k_C$  for self- and cross-combination reactions of  $C_2H$ .



## Cavity Ring Down Spectroscopy of Free Radicals in Atmospheric Flames

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In recent years cavity ring down spectroscopy (CRDS) has been exploited in combustion research for the determination of absolute densities of relevant species. The CRDS technique is complementary to the widely applied laser-induced fluorescence (LIF) diagnostics. Whereas LIF yields information about the spatial distributions of a specific molecule in a flame, the application of CRDS enables quantitative measurements of molecular densities, which are hard to derive from LIF studies. Thus far, the application of CRDS in combustion has been reported mainly for studies of low pressure flames. At atmospheric pressure problems arise by deflection of the laser beam due to steep temperature gradients and the very narrow flame front thickness, which makes it difficult to spatially resolve the molecular distributions in this most relevant part of the flame.

We present CRDS measurements in two different atmospheric flames: a flat premixed methane/air flame and an oxy-acetylene flame used for diamond deposition. Free radicals that have been investigated are OH, CH, HCO, CH<sub>2</sub>, CN and C<sub>2</sub><sup>\*</sup>. In the flat flame we were able to resolve the radical distributions across the flame front with a thickness of 0.5 mm at less than 1 mm from the burner plate. In this flame the CRDS studies were mainly performed on CH. The obtained axial density profile has been compared to numerical simulations based on the GRI-Mech 2.11 and 3.0 reaction mechanism. A good agreement was obtained for the absolute CH densities. However, the maximum CH density was found at a significantly lower temperature than predicted (at about 1600 versus 1750 K), indicating that the reaction mechanism is still not complete for CH. In the same flame measurements have been performed on HCO and CH<sub>2</sub>, which were found in very narrow regions even closer to the burner plate than CH, as expected.

In the oxy-acetylene flame CRDS was applied to study relations between the properties of the grown diamond layers and the distributions of CH and CN above these layers during deposition. In order to determine the local absolute densities the Abel inversion technique was used. The results have been compared to LIF measurements on these species in the same flame, showing a reasonably good agreement. We also succeeded in the determination of excited C<sub>2</sub>(A<sup>1</sup>Π<sub>u</sub>) radicals in this flame by CRDS.

In addition we will present CRDS measurements on NO and NO<sub>2</sub> in the exhaust gas of a diesel engine. It will be shown that concentrations of these molecules in the ppm range can be measured despite of the perturbing presence of soot particles.

## INTRACAVITY LASER SPECTROSCOPY OF NICKEL CHLORIDE: SYSTEM H

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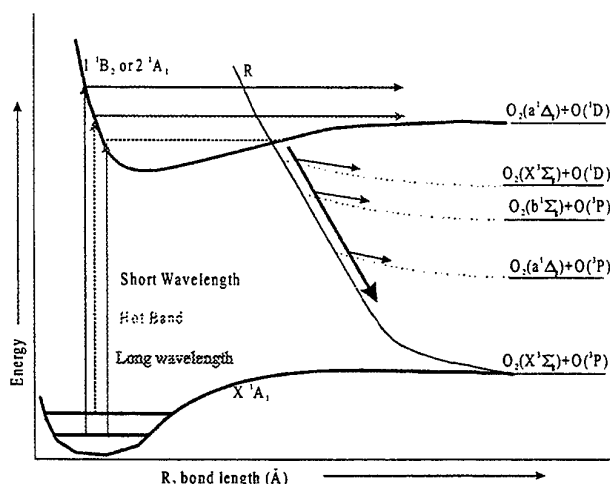
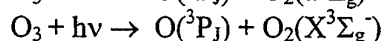
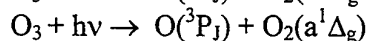
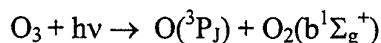
The (0,0) vibronic band of NiCl System H near  $12259\text{ cm}^{-1}$  was recorded at high-resolution in absorption using intracavity laser spectroscopy (ILS) and in emission by Fourier transform (FT) spectroscopy. Originally assigned as the (1,1) vibronic band of a  $^2\Pi_{3/2} - X^2\Delta_{5/2}$  transition, we have shown that this transition is the (0,0) vibronic band associated with a newly identified  $^2\Sigma^+$  excited state and the  $X^2\Pi_{3/2}$  ground state. The molecular constants for the new  $^2\Sigma^+$  electronic state were derived from the rotational analysis. For the ILS absorption spectra, the NiCl molecules were produced in a nickel hollow cathode, operated with a small amount of  $\text{CCl}_4$ . Line positions were referenced to iodine spectra observed from a heated extracavity cell using the intracavity laser as the light source. For the FT spectra, excited NiCl molecules were produced in a King-type carbon tube furnace.

## Ozone Photodissociation in the Huggins Band

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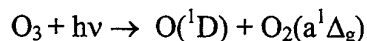
The photolysis of ozone in the Huggins Band between 308nm and 326nm has been studied. By selectively probing  $O(^3P_J)$  photofragments via resonance enhanced multiphoton ionisation (REMPI), time of flight profiles have been obtained which show discrete product channels at these photolysis wavelengths, each channel possibly associated with three different electronic states of the  $O_2$  cofragment, namely:



Time of flight profiles have been taken at various photolysis wavelengths, both on and off vibronic band peaks in the  $O(^3P_J)$  photofragment yield spectrum, and the effect on branching ratios observed.

Further insights into the nature of the dissociation have been obtained by probing the  $O_2(a^1\Delta_g)$  photofragment, which may be formed in coincidence with  $O(^3P_J)$  at these wavelengths, and is also a product of collisional relaxation of the  $O_2(b^1\Sigma_g^+)$  state, another possible  $O(^3P_J)$  cofragment.

The same state has been studied following shorter wavelength photolysis in the red end of the Hartley band, where the spin allowed channel dominates:



Here, vector correlation between the parent transition moment  $\mu$ , and the fragments' velocity  $v$ , and angular momentum  $J$  have been measured. The  $(vJ)$  correlation is dependent on rotational state  $N$ , and observation of alternations in its magnitude with even and odd  $N$  will be described.

### Rate coefficients and products of the reactions of SF<sub>5</sub>CF<sub>3</sub> with several positive ions of atmospheric interest in a SIFT apparatus

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An investigation of the bimolecular reactions of several positive ions of atmospheric interest, H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup>, NO<sub>2</sub><sup>+</sup>, O<sub>2</sub><sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, N<sub>2</sub>O<sup>+</sup>, O<sup>+</sup>, CO<sub>2</sub><sup>+</sup>, CO<sup>+</sup>, N<sup>+</sup>, and N<sub>2</sub><sup>+</sup>, with the greenhouse gas SF<sub>5</sub>CF<sub>3</sub> is reported [1]. The thermal rate coefficients and ion product distributions have been determined at 300 K using a selected ion flow tube. H<sub>3</sub>O<sup>+</sup>, NO<sub>2</sub><sup>+</sup>, and NO<sup>+</sup> are found to be unreactive. The reaction with O<sub>2</sub><sup>+</sup> proceeds with a rate coefficient significantly less than the capture value via chemical routes, in which bonds are broken and formed. The other reagent ions, H<sub>2</sub>O<sup>+</sup>, N<sub>2</sub>O<sup>+</sup>, O<sup>+</sup>, CO<sub>2</sub><sup>+</sup>, CO<sup>+</sup>, N<sup>+</sup>, and N<sub>2</sub><sup>+</sup> react with SF<sub>5</sub>CF<sub>3</sub> with reaction rate coefficients close to or at the capture values. With the exception of the reaction with H<sub>2</sub>O<sup>+</sup>, all these efficient reactions occur by dissociative charge transfer, with CF<sub>3</sub><sup>+</sup> and SF<sub>3</sub><sup>+</sup> being the dominant product ions. The branching ratios compare favourably with those obtained from photon-induced dissociation of SF<sub>5</sub>CF<sub>3</sub> [3], with photon energies similar to the recombination energies of the ions in the SIFT study. This indicates that the charge transfer probably occurs at long range. CF<sub>3</sub><sup>+</sup> forms by direct cleavage of the S-C bond in SF<sub>5</sub>CF<sub>3</sub><sup>+</sup>, SF<sub>3</sub><sup>+</sup> probably from dissociation of (SF<sub>4</sub><sup>+</sup>)<sup>\*</sup> following intramolecular rearrangement within the lifetime of (SF<sub>5</sub>CF<sub>3</sub><sup>+</sup>)<sup>\*</sup>. For H<sub>2</sub>O<sup>+</sup>, the observed ion branching ratios suggest that the reaction proceeds via a chemical pathway.

The reaction kinetics of SF<sub>5</sub>CF<sub>3</sub> with cations [1] and with low-energy electrons, studied in a SWARM apparatus [2], suggest that this molecule will be removed from the earth's atmosphere by ionic reactions occurring in the mesosphere.

- [1] C Atterbury, R A Kennedy, C A Mayhew and R P Tuckett, Phys. Chem. Chem. Phys., (2001) **3**, 1949
- [2] R A Kennedy and C A Mayhew, Int. J. Mass Spectrom., (2001) **206**, i-iv
- [3] R Y L Chim, R A Kennedy, R P Tuckett *et al.* J. Phys. Chem. A., (2001) submitted

**Fragmentation of  $\text{SF}_5\text{CF}_3^+$  studied by TPEPICO spectroscopy :  
the  $\text{SF}_5\text{--CF}_3$  bond strength, and atmospheric implications for the  
greenhouse gas  $\text{SF}_5\text{CF}_3$**

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D J Collins and P A Hatherly (*Univ. of Reading, UK*)

A recent paper [1] has suggested that a new anthropogenic greenhouse gas,  $\text{SF}_5\text{CF}_3$ , recently detected in the atmosphere, has the highest radiative forcing of any gas-phase molecule. Using tunable vacuum-UV radiation from a synchrotron in the range 12-26 eV, we have measured the threshold photoelectron and threshold photoelectron – photoion coincidence spectrum of this molecule [2]. The ground state of  $\text{SF}_5\text{CF}_3^+$  is repulsive in the Franck-Condon region, the parent ion is not observed, and the onset of ionisation can only give an upper limit to the energy of the first dissociative ionisation pathway of  $\text{SF}_5\text{CF}_3$ , to  $\text{CF}_3^+ + \text{SF}_5 + \text{e}^-$ . Using a variation of this coincidence spectroscopy, we have determined the kinetic energy released into the two fragments over a range of energies. Using an impulsive model, the data has been extrapolated to zero kinetic energy to obtain a value for the first dissociative ionisation energy for  $\text{SF}_5\text{CF}_3$  of  $12.9 \pm 0.4$  eV. The enthalpy of formation at 0 K of  $\text{SF}_5\text{CF}_3$  is determined to be  $-1770 \pm 47$  kJ mol<sup>-1</sup>, and the dissociation energy of the  $\text{SF}_5\text{--CF}_3$  bond at 0 K to be  $392 \pm 48$  kJ mol<sup>-1</sup> or  $4.06 \pm 0.45$  eV. The implication of this bond strength is that  $\text{SF}_5\text{CF}_3$  is very unlikely to be broken down by UV radiation in the stratosphere.

In addition, over the complete energy range of 12-26 eV, coincidence ion yields of  $\text{SF}_5\text{CF}_3$  have been determined.  $\text{CF}_3^+$  and  $\text{SF}_3^+$  are the most intense fragment ions, with  $\text{SF}_5^+$ ,  $\text{SF}_4^+$  and  $\text{CF}_2^+$  observed very weakly. Energetic constraints require that  $\text{SF}_3^+$ ,  $\text{SF}_4^+$  and  $\text{CF}_2^+$  can only form with  $\text{CF}_4 + \text{F}$ ,  $\text{CF}_4$  and  $\text{SF}_6$ , respectively, so that fragmentation of  $\text{SF}_5\text{CF}_3^+$  to these ions involves migration of a fluorine atom across the S–C bond. The translational kinetic energy release into  $\text{CF}_3^+ + \text{SF}_5$  is also measured at photon energies between 14 and 19 eV, and the results discussed in terms of different dissociation mechanisms of the ground and excited states of  $\text{SF}_5\text{CF}_3^+$ .

[1] W T Sturges *et al.* Science (2000) **289**, 611.

[2] R Y L Chim *et al.* J. Phys. Chem. A. (2001) submitted

## Theoretical study of the electronic spectroscopy of the $\text{SiF}_3\cdot$ free radical

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The vacuum-UV and visible spectroscopy of  $\text{SiF}_4$  using fluorescence excitation and dispersed emission techniques was reported by one of us in 1997 [1]. The fluorescence excitation spectrum was recorded following excitation with synchrotron radiation from the BESSY 1, Berlin source in the energy range 10-30 eV. Different decay channels were identified over this energy range, with emissions due to excited states of  $\text{SiF}_3\cdot$ ,  $\text{SiF}_2$  and  $\text{SiF}_4^+$ . From a spectroscopic viewpoint, the most interesting observation was  $\text{SiF}_3\cdot$  fluorescence in the range 380-750 nm for vacuum-UV photon excitation energies around 13.0 eV. Using the single-bunch mode of the synchrotron, the lifetime of the emitting state in  $\text{SiF}_3\cdot$  was measured to be  $3.9 \pm 0.7$  ns. At the time, no attempt was made to assign the upper state of this visible emission; it was assumed that the lower state was the ground state of  $\text{SiF}_3\cdot$ .

The microwave spectrum of the  $\text{SiF}_3\cdot$  free radical has been reported [2], a low-resolution electronic emission spectrum in the range 400-800 nm reported [3]. Unlike the  $\text{CF}_3\cdot$  radical, however, there have been no high-resolution infrared studies of  $\text{SiF}_3\cdot$ , and no *ab initio* studies of the properties of excited states of this radical. Yet it seems likely that this radical is important in the plasma etching of silicon wafers using fluorine-containing etchant gases.

In this poster, we report *ab initio* CASSCF calculations on the  $\text{SiF}_3\cdot$  radical which show that the observed emission can only be due to the  $\tilde{\text{A}}^2\text{A}_1 - \tilde{\text{X}}^2\text{A}_1$  transition [4]. The vertical separation of these two states is a sensitive function of F-Si-F bond angle in the range  $115^\circ$ - $120^\circ$ . We calculate the electronic transition moment, and the radiative lifetime of the  $\tilde{\text{A}}^2\text{A}_1$  state as a function of bond angle. We show that the experimental lifetime of 3.9 ns is too short to be attributed to this radiative process. We suggest that the lifetime is dominated by rapid internal conversion of  $\text{SiF}_3\cdot \tilde{\text{A}}^2\text{A}_1$  into high vibrational levels of the ground state.

- [1] H Biehl, R P Tuckett, H Baumgartel, *et al.* *J. Chem. Phys.*, (1997) **107**, 720
- [2] M Tanimoto and S Saito, *J. Chem. Phys.*, (1999) **111**, 9242
- [3] M Suto, J C Han, L C Lee and T J Chuang, *J. Chem. Phys.*, (1989) **90**, 2834
- [4] F R Manby, R P Tuckett and P J Knowles, *Chem. Phys. Letts.*, (2001) in press

## Experimental study of the electronic spectroscopy of the $\text{NF}_2\cdot$ free radical

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The vacuum-UV and visible spectroscopy of  $\text{NF}_3$  using fluorescence excitation and dispersed emission techniques is reported [1]. The fluorescence excitation spectrum has been recorded following excitation with synchrotron radiation from the BESSY 1, Berlin source in the energy range 11-30 eV with a resolution of *ca.* 0.05 eV. Dispersed emission spectra are recorded with a 0.2 m UV/visible spectrometer, sensitive over the range 190-700 nm. Emission due to  $\text{NF } b \ ^1\Sigma^+ - X \ ^3\Sigma^-$  at 529 nm is observed for excitation energies between 11.5 and 21.0 eV. Other emissions, believed to be due to transitions between highly-excited states of  $\text{NF}_2\cdot$ , are observed at higher energies, 14.8 to 24.5 eV. This observation, that emissions from a radical produced by cleavage of two bonds (NF) occur at a *lower* excitation energy than from a radical produced from the cleavage of one bond ( $\text{NF}_2\cdot$ ), is rare and surprising.

Using the single-bunch mode of the BESSY 1 source (pulse width *ca.* 200 ps, orbit time 208 ns), lifetimes associated with two of these  $\text{NF}_2\cdot$  bands at 325 and 410 nm are determined to be 12.9 and 13.0 ns, respectively. This common value suggests that these two transitions originate from a common upper state. The data for  $\text{NF}_2\cdot$  emissions is compared with *ab initio* calculations on the positions of low-lying excited states of this radical [2]. We suggest that the observed emissions are due to highly-excited states of  $\text{NF}_2\cdot$ , perhaps originating from electronic states as high as 15 eV above the ground state. These results are significantly different from those obtained for the  $\text{PF}_2\cdot$  radical produced by vacuum-UV photodissociation of  $\text{PF}_3$  [3], where emission from the *low-lying* valence states of  $\text{PF}_2\cdot$  is predominantly observed.

[1] D P Seccombe, R P Tuckett, H W Jochims and H Baumgartel,  
*Chem. Phys. Letts.*, (2001) **339**, 405

[2] Z L Cai, G H Sha, C H Zhang, M B Huang, *Chem. Phys. Letts.*, (1991) **178**, 273

[3] H Biehl, K J Boyle, D P Seccombe, R P Tuckett, H Baumgartel and H W Jochims,  
*J. Chem. Phys.*, (1998) **108**, 857

### Spectroscopy and structure of the $C_3H^-$ anion revealed by photodetachment studies\*

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The  $C_3H^-$  anion is the smallest hydrocarbon anion which, according to *ab initio* calculations can occur in three stable isomeric structures: cyclic ( $^1A'$ ) and two bent conformers ( $^3A''$  and  $^1A'$ ). Except two photoelectron studies leading to the determination of the lowest electron detachment threshold for the chain and the ring isomer, no spectroscopic experimental data were reported to date. Interest in the  $C_3H^-$  ion stems also from the central role played by neutral  $C_3H$  and the isoelectronic  $C_3H_2$  molecules in the chemistry of the interstellar media.

In the present studies, negatively charged carbon species were generated by an electric discharge in allene and  $d_6$ -benzene diluted in the argon and cooled the supersonic jet expansion. The photodetachment studies were performed on the mass selected  $C_3H(D)^-$  near the photodetachment threshold associated with the chain conformer. The photodetachment spectra can be unambiguously assigned to the  $^3A'' \leftarrow X^3A''$  electronic transition on the basis of vibrational and rotational analyses. All active vibrational modes can be identified and assigned on the basis of *ab initio* calculations. Furthermore, the observation of the vibrational progression leads to determination of the one-dimensional potential curve in the ground and excited states along the CCH bending coordinate. The rotationally resolved spectra provide rotational constants for the ground and excited states. The excited state possesses dipole bound state character, but its geometry is significantly different to that of the parent neutral ground state. The strong perturbation of the neutral core by a dipole bound electron is accounted on the Renner-Teller interaction.

The electron catalyzed isomerization process proposed for the formation of cyclic  $C_3H$  in interstellar media through the electron collision with  $C_3H$  chain molecule is re-considered in the light of the present results. The observation of dipole bound states of  $C_3H^-$  can also be considered as the test for the dipole bound state hypothesis proposed to explain origin of the diffuse interstellar bands and provides evidence of the mechanism for the formation of the stable anion in ISM.

\*M. Pachkov, T. Pino, M. Tulej, and J. P. Maier, Mol. Phys. 2000, in press



**Cation spectroscopy and molecular properties of the selected rotamers of  
hydroquinone and *p*-dimethoxybenzene by mass-analyzed threshold ionization  
spectroscopy**

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**Abstract**

Mass analyzed threshold ionization (MATI) spectroscopy in conjunction with two-color resonant two-photon excitation was used to investigate the ionic properties of the selected conformers of hydroquinone (HYQ) and *p*-dimethoxybenzene (PDMB). The adiabatic ionization energies were determined to be  $64051 \pm 5$ ,  $63998 \pm 5$ ,  $60772 \pm 5$ , and  $60563 \pm 5$   $\text{cm}^{-1}$  for *cis*-HYQ, *trans*-HYQ, *cis*-PDMB, and *trans*-PDMB, respectively. The active vibrations of the HYQ and PDMB cations include the in-plane ring deformation, CC stretching, and CH bending motions. The present experimental results are well supported by ab initio and density functional theory calculations.

(as a poster presentation for 26<sup>th</sup> INTERNATIONAL SYMPOSIUM ON FREE  
RADICALS, September 2-7, 2001 - "La Cittadella", Assisi, ITALY)

### Three-dimensional product scattering distributions from velocity-map ion images from photoinitiated bimolecular reactions in a co-expanded beam

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Velocity-map ion imaging has proved to be a powerful technique for elucidating photodissociation dynamics, and more recently has shown promise as a detection method in studies of bimolecular reactions. In the apparatus we are currently setting up for pump-probe studies of photoinitiated bimolecular reactions, photolysis precursor and target molecule are co-expanded in a supersonic jet. Photolysis of the precursor by a polarised UV laser pulse leads to the formation of a translationally hot atom, which undergoes reactive collisions with the target molecule in the jet. Reaction products are ionized by a second laser pulse and focused onto an imaging detector. We show how the theoretical framework used to extract dynamical information from Doppler-resolved laser induced fluorescence profiles of chemical reaction products can be adapted for use in the analysis of product velocity-map ion images from such an experiment. Product differential cross sections and translational energy release distributions are reliably returned from the images, and in principle it should be possible to investigate the full range of vector correlations between reactant and product velocities and product rotational angular momenta accessible by the Doppler technique.

**Time-Resolved Submillimetre-Wave Spectroscopy of Radicals Produced by Pulsed Discharge and Excimer Laser Photolysis.**

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Atmospheric pollution leads to chains of linked reactions involving radicals created by solar photolysis. A number of these reaction chains are not well understood and require experimental verification of the models. The first step is the spectral characterization of the intervening species. Excimer-laser photolysis due to its specificity is a very good method for creating radicals in the laboratory. These lasers provide high power UV-radiation at several wavelengths suitable for the photolysis of a wide number of precursors. Since they are pulsed it is essential to use *kinetic* detection of the absorption spectrum. For this, a time-resolved signal is recorded at each frequency point during the scan of the BWO providing the submillimetre radiation. This signal is then treated by computer to provide simultaneously two separate spectra; one of stable molecules present in the absorption cell and the other of created reactive molecules within a certain lifetime range. This allows the precursor spectrum to be eliminated and greatly facilitates the identification of new species. The method has been successfully employed to study  $\text{CBr}^1$  and  $\text{HCB}^2$  created by photolysing bromoform at 193 nm.

The pulsed nature of the laser also allows us to obtain information on the lifetime of reactive species under various conditions and could lead to the use of rotational spectroscopy for chemical kinetics.

A less specific but more universal method for creating reactive molecules is that of electric discharge. Although it is often difficult to identify specific species created by this method (because of the high number of possible products) a pulsed discharge may be used for studying the lifetime of molecules for which the spectrum is already known. This method has recently been used to compare the lifetime of FPO and FPS.<sup>2</sup> The results showed a surprising difference with lifetimes of respectively 8 ms and 2 s under the same conditions.

<sup>1</sup> M. Hassouna, A. Walters, C. Demuynck, and M. Bogey, *J. Mol. Spectrosc.* **200**, 16-24 (2000)

<sup>2</sup> First measured by thermolysis of precursors  $\text{F}_2\text{PXF}_2$  (X = O, S) produced at Wuppertal. Acknowledgements to: H. Beckers, H. Bürger and P. Paplewski.

## The O(<sup>1</sup>D) Reaction with Cyclopropane: *Multiple Channel Dynamics*

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### Abstract

Universal crossed molecular beam technique, based on electron impact ionization of chemical products, has been very important in investigating the dynamics of bimolecular chemical reactions experimentally during the last few decades. Products angular and kinetic energy distributions can be measured using this powerful method. In principle, electron impact ionization with quadrupole mass selection is an ideal universal detection method for all reaction products. However, the detection efficiency of the so-called universal detector is quite low because of the low ionization efficiency, the limited quadrupole transmission efficiency, and sometimes the high background in the detector. Recently, much improved detection efficiency for universal detection has been achieved in order to investigate more complicated chemical reactions. A custom designed, larger sized quadrupole mass filter was installed in an effort to increase the transmission efficiency for product ions. A much lower background in the detector was also achieved using modern vacuum technologies. The detection efficiency is improved significantly for all reaction products. This much-improved instrument provides a new exciting tool for investigating the dynamics of more complex reactions with multiple pathways in molecular beam conditions.

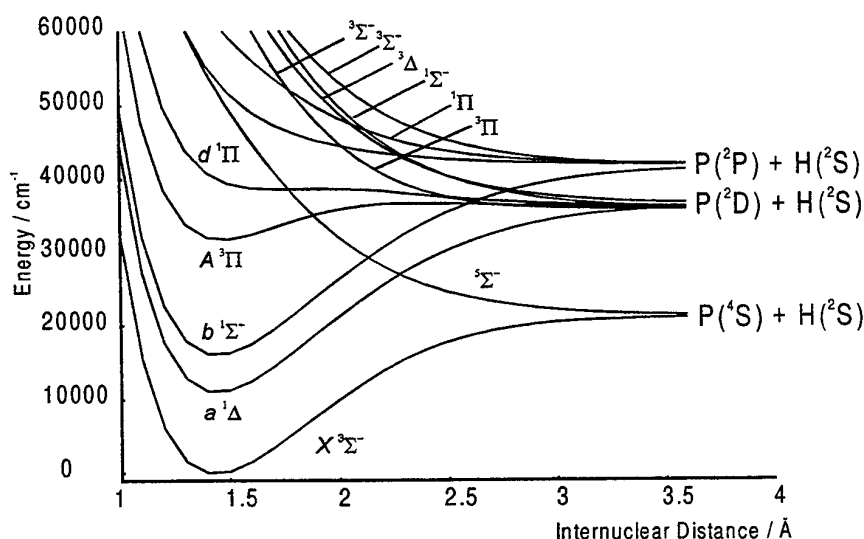
In this report, the O(<sup>1</sup>D)+C<sub>3</sub>H<sub>6</sub> reaction has been investigated using the universal crossed molecular beam technique. Five reaction pathways have been observed for this reaction. In addition to the OH + C<sub>3</sub>H<sub>5</sub> channel, two micro channels for the H<sub>2</sub>CO/HCOH + C<sub>2</sub>H<sub>4</sub> process and the C<sub>3</sub>H<sub>5</sub>O + H channel are clearly observed. A minor H<sub>2</sub> formation channel also seems to be present. Angular resolved time-of-flight spectra have been measured for the observed reaction products in a single set of experiments. Different product angular distributions were measured for the observed product channels, indicating that the detected reaction pathways occur with distinctive dynamics. Branching ratios for all observed reaction channels are also estimated.

## Predissociation dynamics in the $A^3\Pi(1,0)$ band of the PH radical: An experimental and *ab initio* investigation.

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An investigation of the predissociation dynamics of the  $A^3\Pi - X^3\Sigma^-$  system of Phosphinedene has been undertaken. A study by Gustafsson et al [1] on the  $v'=0$  state found predissociation arising from a spin-orbit induced mixing with the  $^5\Sigma^-$  state correlating to ground state atomic fragments. The  $v'=1$  state, investigated for the first time here, shows a strong  $\Omega$ , parity and  $J$  dependence to the lifetime, with low  $J\Omega=0$   $e$  parity levels being much longer lived than all the others. We present both experimental measurements of the lifetimes, using laser induced fluorescence, and purely theoretical Fermi golden rule calculations on *ab initio* potential energy surfaces. MOLPRO 2000 was used to calculate all of the adiabatic potentials correlating to the first three atomic asymptotes at the CASSCF and MRCI level using a selection of basis sets. The potentials for the  $X$ ,  $A$  and repulsive states and the spin-orbit coupling matrix elements between them were calculated with a fine (0.02Å) grid at the MRCI level, and used as input to BCONT 2.0 [2] to calculate the predissociation rates. A CASSCF survey using a VQZ basis set of all the electronic states correlating to the first three atomic asymptotes is shown below. Potentials adjusted to reproduce the experimental data will be presented, though the agreement between experiment and the purely *ab initio* calculations was remarkably good.



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# Experimental and Theoretical Studies on the N and SF<sub>2</sub> Reaction

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We have investigated the detailed electronic band systems of SF<sub>2</sub> radical by the resonance-enhanced multiphoton ionization (REMPI) spectroscopy [1].

In this paper, we report experimental and theoretical studies on reaction of N atom and SF<sub>2</sub> radical. N and SF<sub>2</sub> were produced by dc electric discharge. The products were detected by time-of-flight mass spectrometer using the REMPI method. *Ab initio* quantum chemical calculations were carried out for optimized geometries and energies of reactants, products and intermediate. The electronic excited states of NSF were also calculated. The relative reaction mechanism was explained.

A vibrationally resolved REMPI excitation spectrum by measuring the m/z 46 (NS<sup>+</sup>) ion signal as a function of laser wavelength, were obtained and shown in Fig. 1.

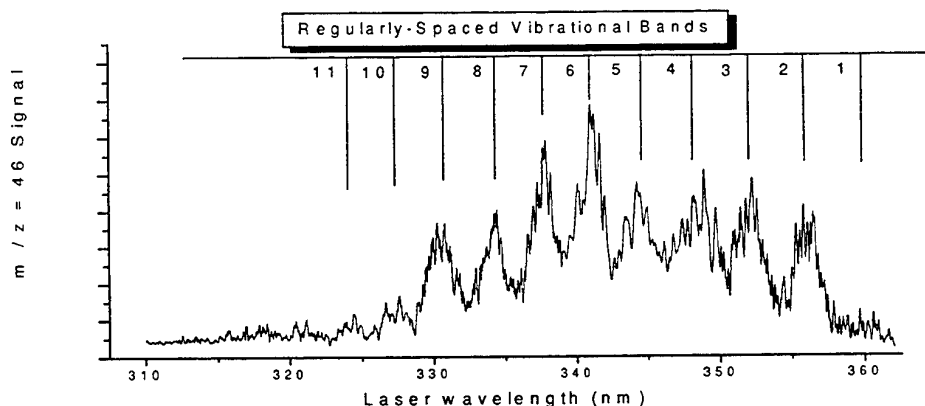


Fig. 1 REMPI excitation spectrum of m/z 46 ion signals between 320 and 360 nm

However, contrasted with the (2+1) REMPI excitation spectrum  $\tilde{F}^2\Delta(3d\delta) \leftarrow \tilde{X}$  of NS radical between 320 and 360 nm [2], our REMPI excitation spectra is completely different. Furthermore, rotationally resolved spectrum of the peak 6 in Fig.1 is far from typical rotational spectrum of NS. It is undoubted that NS is not the spectral carrier of the REMPI excitation spectrum of Fig. 1.

The *ab initio* calculations at DFT B3LYP/6-311+G(d) level show that favorable channel of reaction is as following: excited state N atom (<sup>2</sup>D) and SF<sub>2</sub> (<sup>1</sup>A<sub>1</sub>) radical first form intermediate NSF<sub>2</sub> (<sup>2</sup>A'), then NSF<sub>2</sub> yields products NSF (<sup>1</sup>A') and F (<sup>2</sup>P). The energies of intermediate and products are lower 120 kcal/mol and 92 kcal/mol than reactant, respectively.

The optimized geometries and energies of several excited states of NSF were also calculated in CIS/6-311+G(d) level. The energy 6.77 eV of fourth excited state <sup>1</sup>A'' of NSF is very close to experimental value 6.88 eV from Fig. 1.

It is confirmed from this calculation that NS obtained in experiment was produced by multiphoton ionization and dissociation of NSF. The REMPI excitation spectrum can be assigned a two-photon resonant transition from the ground state to the <sup>1</sup>A'' state of NSF molecule.

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## High-Resolution Rotational Spectrum of the Fluoroformyloxyl Radical in the Gas Phase

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The fluoroformyloxyl radical,  $\text{FCO}_2^*$ , could play a significant role in atmospheric chemistry. Moreover, evidence exists that it has a relatively long lifetime (around 0.3 s)<sup>1</sup> at atmospheric pressure making it a good candidate for direct atmospheric detection. The vibrational spectrum of  $\text{FCO}_2$  trapped in inert gas matrices<sup>2</sup> and its electronic spectrum<sup>3</sup> have already been studied. We report the first observation and analysis of submillimeter-wave transitions of this radical, in the ground electronic state ( $X^2B_2$ ) from  $J = 19 \leftarrow 18$  up to  $J = 30 \leftarrow 29$ .

The fluoroformyloxyl radical was generated by vacuum pyrolysis of  $\text{FC(O)OOC(O)F}$  in a flow system at the entrance of a 2-m-long absorption cell. The cell was surrounded by a solenoid which provided a test on the paramagnetism of the detected species. We have measured and tested more than 300 lines in the spectral region from 241 GHz up to 379 GHz. The lines were mostly split into four components by spin-rotation and spin-spin interactions. Transitions with even  $K_a$  were missing due to the symmetry of the  $^2B$  state and the two symmetric oxygen nuclei. Molecular ground state constants were determined and compared with *ab initio* calculations performed at the CCSD(T) level of theory with polarised-valence-triple-zeta basis set TZ2Pf including correlation of all electrons.

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**H-atom product channel in photodissociation of vinoxy radical via the  $\tilde{B}^2A''$  state**Kesheng Xu, Gabriel Amaral, and Jingsong Zhang\**Department of Chemistry, University of California**Air Pollution Research Center, University of California**Riverside, CA 92521**U. S. A.*

Photodissociation dynamics of jet-cooled vinoxy radical in the photon energy region of 308-325 nm are studied by using the Rydberg H-atom time-of-flight technique. The vinoxy radical beam is produced by 193.3-nm photolysis of ethyl vinyl ether followed by supersonic expansion. Upon excitation into the  $\tilde{B}^2A''$  state by the near-UV radiation, the H + CH<sub>2</sub>CO channel in vinoxy photodissociation is observed. Product center-of-mass translational energy distributions at all the photolysis wavelengths in this study are essentially the same; they are structureless statistical-like distributions, peaking at  $E_T \sim 10$  kcal/mole and with an average translational energy release  $\langle E_T \rangle \sim 0.26E_{\text{avail}}$ . Product angular distributions are isotropic at all the photolysis wavelengths. The obtained dynamic information is consistent with an unimolecular dissociation pathway for the H + CH<sub>2</sub>CO product channel, which presumably occurs after internal conversion from the  $\tilde{B}$  state to the ground state of vinoxy.<sup>1</sup> Action spectra of the H atom products are also obtained in this near-UV region.

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**Laser-induced thermal gratings applied to the detection of NO<sub>2</sub>**

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Various four-wave mixing techniques have been used for non-intrusive determination of temperature and concentration species. A technique based on laser-induced thermal gratings (LITGs) was observed and theoretically investigated by several laboratories [1,2]. Arising from the interference of two laser beams tuned to a resonant wavelength, these interferences generate a spatially periodic and transient grating. Then fast relaxation processes convert the input energy to the bath and lead to the formation of a thermal grating. The efficiency of the scattering of a probe laser pulse on the pumps interference pattern is measured to perform a diagnostic. These techniques have been used for concentration, velocity or temperature measurements of stable and transient molecules in a variety of environments.

At Onera, concentration measurements were performed on nitrogen dioxide using laser-induced thermal gratings (LITGs) in a cell and a free jet. We have studied the properties of the thermal grating signal in order to determine the influence of thermodynamical conditions (pressure, colliders, NO<sub>2</sub> concentration) and the influence of the laser performances (laser bandwidth, beams polarization, pulses energy, delay between pump and probe pulses).

Thermal gratings have proved to be a sensitive tool in environments mainly dominated by collisions (high pressure, combustion...). Further investigations on the influence of the temperature on characteristic decay time need to be undertaken. By tuning the pump laser frequency, the recording of NO<sub>2</sub> spectra through laser-induced thermal grating spectroscopy (LITGS) may provide important informations on the effect of electronic resonances and relaxation processes on the formation of the thermal grating. Theoretical work is in progress to investigate and reproduce these effects.

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## Spectroscopy and Dynamics of the NH-Ne van der Waals Complex.

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The NH-Ne van der Waals complex has been observed in conjunction with the  $c^1\Pi-a^1\Delta$  transition of NH. Low-resolution LIF spectra ( $0.5\text{ cm}^{-1}$  linewidth) exhibit at least three vibronic bands of the complex in the region of the monomer 0-0 band. The complex bands are spread over a region approximately  $30\text{ cm}^{-1}$  wide. The lowest energy band is red-shifted relative to the monomer, indicating that the van der Waals bond strengthens on electronic excitation. Spectra recorded at higher resolution ( $0.08\text{ cm}^{-1}$ ) show congested rotational structure.

Potential energy surfaces for the  $c$  and  $a$  states of NH-Ne have been calculated at the CASPT2 level of theory. Calculations performed using  $vtz$ ,  $vqz$ , and  $vpt$  have been used to extrapolate the results to the complete basis set (CBS) limit. These surfaces are being used to predict and interpret the  $c$ - $a$  spectrum. The objective of this effort is to evaluate the suitability of the CASPT2/CBS extrapolation for prediction of the properties of weakly bound open shell complexes.

### The Near-Infrared $Y^2\Sigma^+ - X^2\Pi$ Transition of CuSe

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The diatomic molecule CuSe was observed for the first time. A King-type carbon tube furnace was used to produce the gas phase of the CuSe molecules. The Fourier Transform Spectrometer associated with The National Solar Observatory, Kitt Peak, Arizona was used to record the molecular emission spectrum, occurring near  $11,000\text{ cm}^{-1}$ . A vibronic analysis and comparison of the spin-orbit constant to other Cu-group 16 diatomic molecules are presented.

## The 193-nm Photodissociation of NCO

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The 193-nm photolysis of the NCO radical has been investigated. NCO was generated from the reaction of  $\text{CN} + \text{O}_2$ , where the CN was produced by 193-nm photolysis of  $\text{C}_2\text{N}_2$  close to the nozzle of a pulsed jet. A second 193 nm photon dissociated the NCO radical during the same laser pulse. At this photon energy both the N-CO and the NC-O bonds may break.  $\text{N}(^2\text{D}, ^2\text{P})$  and CO products have been detected using vacuum ultraviolet laser induced fluorescence. A direct measurement of the  $\text{N}(^2\text{D}): \text{N}(^2\text{P})$  branching ratio yielded an upper limit of  $72 \pm 18$ . The CO vibrational distribution was modeled with prior distributions for each of the contributing channels with co-products  $\text{N}(^4\text{S}, ^2\text{D} \text{ and } ^2\text{P})$ . Combination of the results from the prior model and the direct measurement yielded a branching ratio of  $\text{N}(^4\text{S}): \text{N}(^2\text{D}): \text{N}(^2\text{P})$  of  $(5.1 \pm 1.8) : (93.6 \pm 4.8) : (1.3 \pm 0.3)$ . For the  $\text{N}(^2\text{D}) + \text{CO}$  product channel, the average energy disposal into product relative translation (8%) and CO vibration (24%) was determined, leaving 68% of the available energy to appear as CO rotation. This observation suggests that the geometry of the dissociating state of NCO is likely bent.

## Mass-spectrometric study of double photo-ionization of HBr by synchrotron radiation

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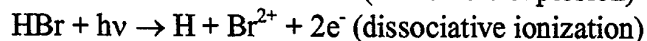
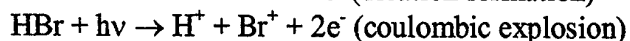
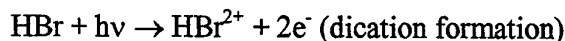
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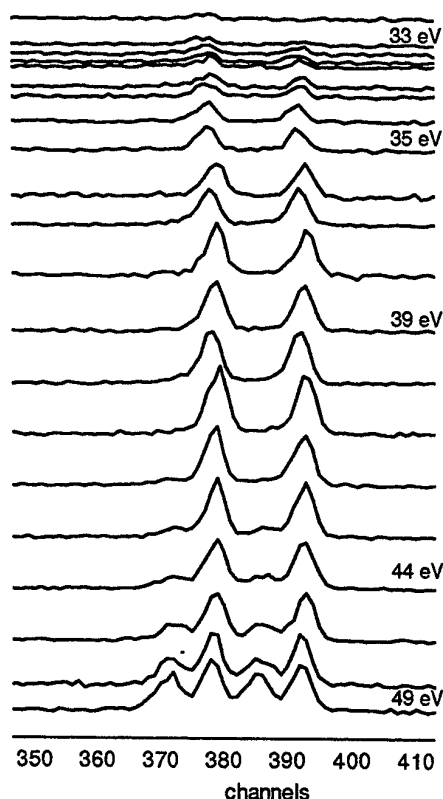
The double photo-ionization of HBr molecules has been studied as a function of the photon energy, by coupling synchrotron radiation with a time-of-flight mass spectrometer (TOFMS). The processes which have been observed are:



The experiment has been carried out in the Gas-phase Beamline at the ELETTRA Synchrotron facility of Trieste. The light source is an undulator with a Variable Angle Spherical Grating Monochromator. The energy selected light beam is crossed with an effusive beam of HBr at room temperature. Product ions of the above processes are analyzed by the TOFMS which uses the electrons emitted during the ionization event and detected by a channel electron multiplier, as start pulses. The ions are then detected by a channel plate multiplier.  $\text{H}^+$  and  $\text{Br}^+$  ions produced by the coulombic explosion have been separated from those also produced by other single ionization events by using a coincidence detection technique.

Threshold energies for the three processes have been measured, while for dication formation and dissociative ionization processes the energy dependence of the branching ratio has been also obtained.

The results are presently under analysis, but they appear in a rather good agreement with *ab initio* calculations of potential energy curves performed by Banichevich et al.<sup>1</sup>.



*Details of the mass spectrum as a function of the photon energy, showing the two isotopic components of  $\text{HBr}^{2+}$ . Note at high energy the appearance of the  $\text{Br}^{2+}$  ions.*

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# FOURIER TRANSFORM MICROWAVE STUDIES OF FREE RADICALS RELEVANT TO COMBUSTION AND ATMOSPHERIC CHEMISTRY

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We report on the application of a Molecular Beam-Fourier Transform Microwave (MB-FTMW) spectrometer for investigations of rotational spectra of free radicals in the spectral region from 8 to 40 GHz. The experimental set-up consists of a near semi-confocal Fabry-Perot microwave resonator mounted in a stainless steel vacuum chamber. The cavity length can be adjusted by moving the spherical mirror. Radicals are generated in a pulsed supersonic free jet expansion in He or Ar either by pulsed excimer laser photolysis or by flash pyrolysis of different precursor molecules. For the laser photolysis source, we use a current actuated slit valve near to the center of the flat mirror just above the microwave antennas. The pyrolysis source consists of a conventional solenoid actuated molecular beam valve to which we attached a resistively heated 1 mm i.d., 45 mm long SiC tube, mounted on the face plate of the valve. The performance of the spectrometer was optimized by recording spectra of SO ( $X^3\Sigma$ ) produced by 193 nm photodissociation of SO<sub>2</sub> in Ar. New results are presented at the conference for a series of carbenes (CF<sub>2</sub>, CCl<sub>2</sub>, CFCl, CHCl) and for the vinoxy radical (C<sub>2</sub>H<sub>3</sub>O) generated by laser photolysis or by flash pyrolysis.

## P-127

# INFRARED LASER SPECTRUM OF THE FUNDAMENTAL BAND OF THE BORON MONOXIDE FREE RADICAL

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The infrared diode laser absorption spectrum of the fundamental band of the boron monoxide (BO) radical in its ground  $^2\Sigma^+$  state has been observed. The source of the radical was the reaction of BCl<sub>3</sub> with O <sup>3</sup>P atoms in the **absence** of molecular oxygen. Fifteen lines of <sup>11</sup>BO and three lines of <sup>10</sup>BO have been measured. The <sup>10</sup>BO lines show a small, partially resolved, doublet structure of about 0.01 cm<sup>-1</sup> which is not present in the <sup>11</sup>BO species. This is attributed to the complex hyperfine pattern expected for the <sup>10</sup>B (I=3) nucleus. The band origins of the two isotopomers are 1861.92465(48) and 1915.30554(16) cm<sup>-1</sup> respectively. Combining the diode laser value of B<sub>1</sub> = 1.756829(11) cm<sup>-1</sup> with the microwave determination of B<sub>0</sub> leads to a value of r<sub>e</sub> = 1.204068(7) Å from the <sup>11</sup>BO spectrum.

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